The Electrolytic Corrosion of Some Metals

A THESIS

By GORRELL ROBERT WHITE

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Electrochemists have paid more attention to the precipitation of metals at the cathode than to the corrosion of metals at the anode. This is not to be wondered at because a good adherent deposit at the cathode is absolutely essential for accurate determinations in electro-analysis and for the success of all processes for the electrolytic refining of metals. For these refining processes, a good even corrosion of the anode with the loss due to mechanical disintegration reduced to a minimum is all that is necessary. In the electro-analysis of metals, these problems do not enter at all because insoluble anodes are always used. As a result of this greater interest in deposition, no systematic study of electrolytic corrosion or dissolution of the anode has been made. However, the anodic behavior of iron,[1] chromium,[2] nickel[3] and cobalt[4] has been studied with completeness to throw some light, if possible, on the question of their passivity. The anodic behavior of copper[5] in neutral and acid copper sulphate solutions has also been studied with care.

In this paper, a study has been made of the electrolytic corrosion of zinc, copper, tin, cadmium, iron, and nickel in solutions of sodium acetate, tartrate, chloride, sulphate, and nitrate. As a rule, the concentration of the electrolyte was

[1] Heathcote: Jour. Soc. Chem. Ind., 26, 899 (1907). Byers: Jour. Am. Chem. Soc., 30, 1718 (1908). Schoch and Randolph: Jour. Phys. Chem., 14, 719 (1910).

[2] W. Hittorf: Zeit. Elektrochemie, 4, 482 (1898); 6, 6 (1899); 7, 168 (1900).

[3] LeBlanc and Levi: Boltzmann's Festschrift, 185 (1904); Levi: Gazz. chim. ital., 35, 391 (1905). Schoch: Trans. Am. Electrochem. Soc., 14, 99 (1908). Byers: Loc. cit. Schoch: Am. Chem. Jour., 41, 232 (1909). Schoch and Randolph: Jour. Phys. Chem., 14, 719 (1910).

[4] Byers: Loc. cit.

[5] Wohlwill: Zeit. Elektrochemie, 9, 311 (1903); Foerster: Ibid., 5, 511 (1899).

75 grams of C. P salt per liter. If the salt was hydrated, no correction was made for the water of crystallization. Some experiments were also made with a concentration of 25 grams per liter but no special points of interest were found by this variation of concentration. The electrolysis was carried on at room temperature, unless otherwise specified, in a special stirring device in which it was possible to run five determinations in series. By this device the anode was rotated, thus ensuring a thorough mixing of the anode and cathode products. In every case, before the run was made, the anode was filed, scoured with carborundum paper, rinsed with distilled water and absolute alcohol, dried in air and then in a desiccator over calcium chloride for an hour before weighing. The filing and scouring ensured a clean surface for each run. After weighing, the anode was placed in the electrolyte with a platinum or nickel wire for cathode and a current was passed through for a certain time. In each experiment, the current was determined by a copper coulometer which was run in series with the electrolytic cells. An ammeter was also placed in the circuit for control of the current during the run. The electrolysis at room temperature was carried on in 200 cc of electrolyte placed in thick-walled glasses to prevent breakage. The electrolysis was conducted without porous cups, so the electrolyte and the resulting precipitate were subjected to the action of the gases liberated at the electrodes. The anodes and the cathode of the coulometer were always kept in desiccators both before and after electrolysis to protect them from moisture and oxidation.

At the conclusion of the run, the cathode of the coulometer was rinsed with distilled water and absolute alcohol, allowed to dry in air and then in a desiccator for an hour and the gain in weight determined. The cathode was never dried with bibulous paper nor heated to remove the water and alcohol. By following this procedure, the weight of the cathode did not change, even on standing in the desiccator for extended periods of time. The anodes were cleaned by removing the adhering precipitate with a glass rod covered with rubber tubing, by

rubbing with a piece of wood or by a stiff bristle brush. Chemicals were never used in removing the precipitate from the anode. After the anode had been cleaned as thoroughly as possible by the methods specified, it was rinsed with water and absolute alcohol, dried in air and then in a desiccator for an hour and the loss in weight determined. By expenditure of time and energy, the adhering hydroxide could be removed almost completely from the anode. This method does not give the actual loss because some of the precipitate is certain to adhere. There will, however, always be some loss at the anode due to mechanical disintegration and this will appear in the results as corrosion. These two errors tend to compensate each other. If the corrosion was higher than expected, the precipitate was examined to see if any pieces of metal had dropped off. As a further check, the precipitate was dissolved in dilute acetic acid and then hydrochloric acid was added to see if any gas was given off by the particles which did not dissolve in acetic acid. As a rule, there was little or no gas evolution to indicate the presence of metallic particles. There was never enough of the metal present in the precipitate to account for the excess corrosion. Wohlwill[1] has shown that with copper electrodes in sulphuric acid the loss by mechanical disintegration may reach 23 percent. In all of the cases studied, the loss due to this cause never reached this figure and is, in fact, very small.

The results given in the subsequent tables are expressed as percentage current efficiency. The theoretical anode loss is calculated from the following proportion: equivalent weight of copper (31.8): equivalent weight of metal X = gain in weight of copper cathode: loss in weight of the anode of metal X. Theoretically, the gain in weight at the cathode should just equal the loss in weight at the anode. In the proportion above, it is assumed that this is true. As a matter of fact, the anode loss in the copper coulometer is always greater than the cathode gain because some of the copper

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[1] Wohlwill: Zeit. Elektrochemie, **9**, 311 (1903).

dissolves as the cuprous salt as Foerster and Seidel[1] and Richards,[2] Collins and Heimrod have shown. On the other hand, the anode loss may be very much less than the theoretical cathode gain as shown by all the metals which become passive. The ratio of the theoretical, *i. e.*, 100 percent loss at the anode and the actual loss will give the percentage current efficiency of the corrosion.

The coulometer solution was made up of 150 grams of crystallized copper sulphate, 50 grams of concentrated sulphuric acid and 50 grams of alcohol dissolved in a liter of water. The addition of alcohol is said by Oettel[3] to be especially advantageous if currents of less than one ampere are to be used. The size of the cathode depended on the current strength and was always well within the limits given by Foerster,[4] *i. e.*, not more than 0.02–0.03 and not less than 0.005 ampere per sq. cm of surface. When the current was small, only one anode was used; but, with larger currents, the cathode was suspended between two anodes. Some comparison runs were made with one and with two anodes in the coulometer. It was found that the increase in weight of the cathode was the same in each case for currents of 0.3–0.5 ampere. As an extra precaution, the anode was cleaned with nitric acid and rinsed with distilled water before beginning a run. As a result of the precautions taken, very bright and adherent deposits were obtained. If the deposit was not satisfactory, the run was rejected. The results with the copper coulometer are sufficiently accurate for this work because according to Lehfeldt[5] an accuracy of 0.2–0.3 percent can be obtained without taking any special precautions. If the coulometer is to be used for determining the current, the time must be recorded. One ampere passing through

[1] Foerster and Seidel: Zeit. anorg. Chem., **14**, 106 (1897).

[2] Richards, Collins and Heimrod: Zeit. phys. Chem., **32**, 321 (1900).

[3] Oettel: Chem.-Ztg., **17**, 543, 577 (1893).

[4] Foerster: "Electrochemie wässriger Lösungen," p. 41.

[5] Lehfeldt: "Electrochemistry," Vol. I, p. 10.

the solution for 1 hour will deposit 1.186[1] grams of copper.

When an attackable metal is made anode in a solution of a sodium salt, the anions liberated there will form the corresponding salt of the metal. If the salt thus formed is soluble, it will diffuse away and will react eventually with the sodium hydroxide which is formed at the cathode. Stirring during electrolysis ensures a complete mixing of the anode and cathode products and in most cases a precipitate of the hydroxide will be formed. Lorenz[2] has, in fact, used this method to prepare the hydroxides of several metals. The anode has a very characteristic appearance which depends on the metal and the electrolyte.

Zinc

The corrosion of zinc was first studied under the conditions previously described. The zinc anodes were made from zinc rods which contained a trace of iron but were free from arsenic and carbon. The electrodes were numbered and were changed around from one electrolyte to another in successive runs to obviate any possibility of the surface of the metal influencing the results. Thus, if comparable results were obtained by using different anodes in the same electrolyte, it is presumable that the corrosion noted is due to the electrolyte and not to the electrode. Suppose an electrode is composed of metal which corrodes very easily and this is made anode in one electrolyte constantly, the results would show a greater efficiency of corrosion than is actually due to the electrolyte. By changing the electrodes, results closer to the average corrosion in a given electrolyte will be obtained.

A very important factor in all the work is the condition of the anode surface. During one run a surface may be exposed to the electrolytic action which dissolves readily while during the next run the surface may be very resistant to attack. Metals are seldom homogeneous and any segregation of the impurities, any difference due to the size of the

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[1] Richards, Collins, and Heimrod, Loc. cit., give 0.00032915–0.00032925 gram per ampere second or 1.18494–1.18530 grams per ampere hour.

[2] Lorenz: Zeit. anorg. Chem., **12**, 436 (1896).

crystals, or any difference brought about by stress during cooling in the mould may affect the rate at which corrosion takes place. According to Andrews, the effect of stress on iron is to cause the metal to dissolve less readily. The same results were obtained by Walker and Dill[1] with Swedish iron in a solution containing ferrous sulphate and potassium chloride when the iron was subjected to stresses up to 31,000 pounds per square inch. This effect is at best very small and doubtless has little or no influence on the corrosion of metals under the conditions holding in this work.

The results of the electrolysis with the larger current were as follows: In the chloride, sulphate and acetate solutions, a heavy white precipitate of zinc hydroxide was formed. The anode surface, after the adhering hydroxide and a thin, black, non-adherent film were removed, was flaky and clean but very slightly darkened. In the tartrate solution, no precipitate was formed because the hydroxide is soluble in sodium tartrate. The anode was coated with a black adherent layer; and a hard white ring, which can be removed, was formed at the surface of the electrolyte. In the nitrate solution, a white precipitate was formed. The anode was pitted with very small depressions which were filled with the white precipitate and presented a "speckled" appearance. It was difficult to remove all this hydroxide, and this fact may account for the lower values obtained for the corrosion in this solution. In all five electrolytes, spongy metallic zinc was formed at the cathode. The filtered supernatant liquid in all cases was alkaline to litmus paper. This may be due to selective adsorption of the acid radical by the colloidal precipitate, thereby leaving the supernatant liquid alkaline. Sodium acetate and tartrate are, of course, alkaline to litmus. Hydrogen was evolved at the cathode in all the solutions. With sodium nitrate, the quantity of hydrogen evolved was small and it was found that nitrites were formed by this cathodic reduction. This reduction would be aided by the presence of the spongy zinc at the cathode. The presence

[1] Walker and Dill: Trans. Am. Electrochem. Soc., 11, 153 (1907).

of this zinc at the cathode may be due either to reduction of the hydroxide by the nascent hydrogen or to the formation of some zincate from which the zinc would be precipitated by the current.

The following table gives the numerical results for the zinc with the larger current. The actual loss in weight and the percentage efficiency of corrosion as calculated by the above proportion are given. The subscripts are the electrode numbers and the order in which the test piece was anode in the different electrolytes may be followed.

TABLE I—ZINC

At. wt. 65.4; equivalent weight, 32.7
Average anode surface, 12.5 cm^2

Run	Cathode coulometer	100 percent Zn	Time	C. D. amp/dm^2
1	0.5252	0.5401	1 hr.	3.5
2	0.4278	0.4399	1 hr.	2.9
3	0.3998	0.4111	1 hr.	2.7
4	0.6805	0.6998	1 hr.	4.6
5	0.3526	0.3626	1 hr.	2.4

Run		NaCl	Na$_2$SO$_4$	NaNO$_3$	NaC$_2$H$_3$O$_2$	Na$_2$C$_4$H$_4$O$_6$
1	g.	0.5486$_1$	0.5494$_2$	0.5228$_3$	0.5496$_4$	0.5468$_5$
	%	101.6	101.7	96.8	101.7	101.2
2	g.	0.4494$_1$	0.4492$_2$	0.4304$_3$	0.4462$_4$	0.4056$_5$
	%	102.2	102.1	97.8	101.4	92.2
3	g.	0.4164$_4$	0.4214$_5$	0.3608$_1$	0.6694$_3$	0.3932$_2$
	%	101.3	102.5	87.8	162.8	95.6
4	g.	0.7092$_4$	0.7116$_5$	0.7684$_1$	0.7242$_3$	0.5846$_2$
	%	101.3	101.7	109.8	103.5	83.5
5	g.	0.3684$_1$	0.3710$_4$	0.2900$_3$	0.3674$_6$	0.3516$_5$
	%	101.6	102.4	80.0	101.3	97.0

The electrolysis was run on the 110 volt direct current which fluctuates markedly because of a variable load, due to turning on and shutting off projection lanterns. This accounts in part for the difference in the amounts of copper deposited in the coulometer. Any hydroxide which adhered

to the anode would affect the resistance of the circuit and therefore the current.

It will be seen that, in many cases, the percentage corrosion exceeded the theoretical value, 100. This may be accounted for by mechanical disintegration and by "local action" between impurities in the zinc and pure zinc, and by zinc in different physical states. Examination of the precipitates for metallic particles showed that the loss due to this cause was very small and will not account for the excess corrosion. Doubtless, part of this excess corrosion was due to "local action" and there is a faint possibility that some of the metal may dissolve with a lower valence than two which would, of course, increase its electrochemical equivalent.

In run 3, the anode in the acetate solution showed a corrosion of 162.8 percent. The average corrosion was about 102 percent. A very much heavier precipitate of the hydroxide was noted and the amount of mechanical disintegration was small. This large excess may then be due to an easily soluble stratum of metal or to error.

Table II gives the numerical results for zinc with the smaller current.

TABLE II—ZINC

Low current densities

Run	Cathode coulometer	100 percent Zn	Time	C. D. amp/dm^2
1	0.2352	0.2419	5 h. 25 m.	0.3
2	0.1796	0.1847	4 h. 35 m.	0.26
3	0.2018	0.2075	5 h. 30 m.	0.25
4	0.1808	0.1859	5 h.	0.24

Run		NaCl	Na$_2$SO$_4$	NaNO$_3$	NaC$_2$H$_3$O$_2$	Na$_2$C$_4$H$_4$O$_6$
1	g.	0.2464$_5$	0.2456$_3$	0.1866$_4$	0.2382$_1$	0.2128$_2$
	%	101.9	101.5	75.4	98.5	88.0
2	g.	0.1942$_5$	0.1916$_3$	0.1550$_4$	0.2014$_1$	0.1852$_2$
	%	105.2	103.8	66.7	109.1	100.3
3	g.	0.2108$_5$	0.2076$_3$	0.1600$_4$	0.2008$_1$	0.1956$_2$
	%	101.6	100.4	77.1	96.8	94.3
4	g.	0.1876$_5$	0.1842$_3$	0.1448$_6$	0.1742$_1$	0.1840$_2$
	%	100.9	99.1	76.1	93.7	99.0

The general appearance of the anodes was about the same as with the higher current densities and precipitation took place in the same solutions. In the chloride and sulphate solutions, the percentage corrosion was about the same with both current densities. In acetate solution, it was not quite so great with the lower current density as with the higher. In the tartrate solution, the corrosion was about the same in both cases. This is peculiar because sodium tartrate has a marked solvent action on zinc and it would be expected that chemical corrosion would aid the electrochemical and thus give a greater loss on longer exposure to the solvent action of the tartrate. In sodium nitrate, the corrosion by the small current was very much less than by the large.

Copper

The corrosion of copper rods was studied in the same electrolytes, and the effect of concentration and temperature as well as current density was also considered. The copper was 99.93 percent pure. The results with the larger current were as follows: In the chloride solution, the anode was covered with a non-adherent brick-red coating of cuprous oxide which could be easily removed, leaving a bright clean surface. The precipitate was orange-yellow cuprous hydroxide with some red cuprous oxide scattered through. In the sulphate solution, the anode was covered with a non-adherent coating of cuprous oxide, easily removable, leaving a surface which was less bright and clean than the chloride. The precipitate was a dirty green color with blue scattered through. In the nitrate solution, the anode was much like the anode in the sulphate solution but was darker. The precipitate was about the same as in the sulphate solution. In the acetate solution, the anode was clean and bright. The precipitate was blue with some black scattered through. In the tartrate solution, the anode was covered with an olive-green coating which could be removed in part, although some adhered, leaving a darkened surface. At the surface of the electrolyte, a hard adherent blue ring was formed which could be removed com-

pletely, leaving the surface slightly roughened. The olive-green coating increased the resistance of the circuit markedly. No precipitate but a deep blue solution was formed, since copper hydroxide is soluble in alkaline tartrate solution. In all cases, the filtered supernatant liquid was alkaline to litmus paper. At the cathode, some metallic copper was deposited. There was also formed at the cathode some cuprous oxide which was intermixed with spongy metallic copper. This metal may come from the reduction of the hydroxide by hydrogen.

The following table gives the numerical results for copper with the larger current:

<div align="center">Table III—Copper</div>

<div align="center">At. wt. 63.6; equivalent weight, 31.8
Average anode surface, 18 cm^2</div>

Run	Cathode coulometer	100 percent Cu	Time	C. D. amp/dm^2
1	0.449	0.449	1 hr.	2.1
2	0.3996	0.3996	1 hr.	1.8
3	0.5298	0.5298	1 hr.	2.5
4	0.3678	0.3678	1 hr.	1.7

Run	NaCl	Na$_2$SO$_4$	NaNO$_3$	NaC$_2$H$_3$O$_2$	Na$_2$C$_4$H$_4$O$_6$
1	g. 0.7542$_5$	0.4798$_1$	0.5018$_2$	0.1570$_3$	0.2768$_4$
	% 167.9	106.9	111.8	35.0	61.6
2	g. 0.8022$_5$	0.4342$_1$	0.4560$_2$	0.1342$_3$	0.2418$_4$
	% 200.7	108.7	109.0	33.6	60.5
3	g. 1.0722$_3$	0.5606$_1$	0.6098$_4$	0.1672$_5$	0.3800$_2$
	% 202.4	105.8	115.1	31.6	71.7
4	g. 0.7448$_2$	0.390$_1$	0.4234$_5$	0.108$_3$	0.2186$_4$
	% 202.5	106.0	115.1	29.4	59.4

With the smaller current, the appearance of the anodes was somewhat different from that with the larger current. In the chloride solution, the anode was not quite so clean and bright after the red oxide had been removed. In the sulphate solution, the anode was covered with easily removable cuprous

oxide, but the surface was appreciably darkened. In the nitrate solution, the anode was covered with an easily removable green coating, leaving the surface coated with an adherent chocolate-colored oxide. In the acetate solution, the anode was again clean and bright. In the tartrate solution, the anode was striped and had a definite gold color while at the surface of the electrolyte the blue ring was again formed. The cathodes appeared about the same with these current densities as with the higher. The precipitates had the same general appearance in both cases except in the acetate solution where the precipitate was more greenish blue than with the lower current density. The filtered supernatant liquid was again alkaline. In the nitrate solution, nitrite was again found. Nitrites were always tested for by the potassium iodide and acetic acid method.

Table IV gives the numerical results for copper with the smaller current.

TABLE IV—COPPER
Low current densities

Run	Cathode coulometer	100 percent Cu	Time	C. D. amp/dm^2
1	0.2703	0.2703	5 h. 30 m.	0.23
2	0.2944	0.2944	6 hr.	0.18
3	0.2429	0.2429	5 hr.	0.23
4	0.2655	0.2655	5 h. 30 m.	0.23

Run	NaCl	Na$_2$SO$_4$	NaNO$_3$	NaC$_2$H$_3$O$_2$	Na$_2$C$_4$H$_4$O$_6$
1	g. 0.5496$_2$	0.3054$_1$	0.2246$_5$	0.0488$_3$	0.277$_4$
	% 203.3	0.113	83.1	18.1	102.5
2	g. 0.5962$_1$	0.3316$_2$	0.2588$_5$	0.0702$_3$	0.2984$_4$
	% 202.5	112.6	88.0	23.8	101.4
3	g. 0.4992$_6$	0.2752$_7$	0.207$_8$	0.0528$_9$	0.2514$_{10}$
	% 205.5	113.3	85.2	21.7	103.5
4	g. 0.5398$_8$	0.3012$_7$	0.225$_6$	0.0450$_{10}$	0.271$_9$
	% 203.3	113.4	84.7	16.9	102.1

Comparison of the results in Tables III and IV show that with both current densities the corrosion in the chloride

solution was about the same. The efficiency of 200 percent is accounted for by the fact that in chloride solutions copper dissolves at the anode in the cuprous form while the results are calculated with copper as a bivalent metal. Apparently, the corrosion was slightly more efficient with the small current. This may be accounted for to some extent by the solvent action of the electrolyte on the metallic copper, especially on the longer exposure of the electrolyte to the air. Tilden[1] and Carnelley[2] have shown that sodium chloride containing air in solution has a marked solvent action on copper. In the sulphate solution, the corrosion with the lower current density was also somewhat higher than with the higher current density. In the nitrate solution, the corrosion was markedly less with the lower current than with the higher, and this is doubtless due to the formation, with the low current density, of an adherent oxide film which protects the electrode from corrosion. In the tartrate solution, the corrosion with the low current was very much greater than with the higher current and may be explained by the fact that with the latter the oxide or basic tartrate was formed at the anode faster than the sodium tartrate could dissolve it. This substance, by adhering to the anode, cut down the efficiency of the corrosion. In the acetate solution, the corrosion with the large current was appreciably greater than with the small current and in both cases, a clean bright surface resulted after electrolysis.

Some experiments were carried on with electrolytes containing 25 grams of the salt per liter instead of the 75 grams which was used in the other runs. Both high and low current densities were used. With the higher current density, the anodes in the tartrate solution became coated with the olive-green deposits which increased the resistance so much that the current was cut off almost completely. If the current was shut off, the electrodes, on being allowed to stand in the solution, were depolarized, and if the current were turned on again,

[1] Tilden: Jour. Soc. Chem. Ind., 5, 84 (1886).
[2] Carnelley: Jour. Chem. Soc., 30, 1 (1876).

electrolysis took place only to be followed by polarization and complete stoppage of the current. For this reason, it was impossible to obtain any results for the corrosion of copper in this dilute tartrate solution with the higher current density. However, some measurements were made with the dilute solutions of sodium nitrate and sodium acetate. The results are given in the following table with some results for the sodium tartrate solution (75 grams per liter).

TABLE V—COPPER

Run	Cathode coulometer	100 percent Cu	Time	C. D. amp/dm^2
1	0.5968	0.5968	1 hr.	2.8
2	0.3781	0.3781	1 hr.	1.8
3	0.3349	0.3349	1 hr.	1.6

Run	$NaNO_3$	$NaC_2H_3O_2$	$Na_2C_4H_4O_6$ (75 grams per liter)
1	g. 0.6349_2 % 106.4 g. 0.642_5 % 107.6	0.4734_3 79.3	
2	g. 0.4212_8 % 111.4	0.2179_{10} 57.6	0.2158_6 57.1 0.2403_9 63.5
3	g. 0.4045_{10} % 120.8	0.2175_7 64.9 0.233_8 69.6	0.2022_6 60.4 0.217_9 64.8

The corrosion in sodium nitrate solutions of both concentrations was about the same. The corrosion in the dilute sodium acetate solution was much greater than in the more concentrated solution. The appearance of the anode was about the same in both concentrations of the nitrate. The anode in the dilute acetate solution was pitted and darkened slightly, but still fairly clean.

Runs were also made with copper anodes in the dilute solution with the low current density. The results follow.

TABLE VI—COPPER

Run	Cathode coulometer	100 percent Cu	Time	C. D. amp/dm^2
1	0.1929	0.1929	5 hr.	0.18
2	0.2388	0.2388	6 hr.	0.19

Run	NaNO$_3$	NaC$_2$H$_3$O$_2$	Na$_2$C$_4$H$_4$O$_6$
1	g. 0.157$_5$ % 81.4 g. 0.1542$_1$ % 79.9	0.1794$_3$ 93.00 0.1664$_2$ 82.3	0.1966$_4$ 104.3
2	g. 0.1835$_1$ % 76.8	0.1787$_8$ 74.8 0.1778$_7$ 74.4	0.2585$_{10}$ 108.2 0.1981$_6$ 82.9

With the small current density, the tartrate showed no tendency to polarize and dissolved with high efficiency, giving a good clean anode surface and a deep blue solution. In run 2, with anode 6, the resulting solution was not clear but contained a suspension of cuprous hydroxide. The anode surface was not as clean as those in the other runs. The corrosion efficiency in sodium nitrate was again lower with the low current density and the adherent chocolate-brown oxide was again formed on the anode. The corrosion in sodium acetate showed fluctuation but was somewhat higher with the small current than with the large current. This behavior is just the reverse of the behavior in the more concentrated solution.

Effect of Increased Temperature

It has been shown by Richards, Collins and Heimrod[1] that copper, when heated with copper sulphate in the warm limb of their "circulation apparatus," is dissolved with the formation of cuprous sulphate which decomposes in the cold limb with the liberation of metallic copper and the reforma-

[1] Loc. cit.

tion of cupric sulphate. The reaction is reversible and is represented by the following equation:

$$Cu + CuSO_4 \rightleftarrows Cu_2SO_4.$$
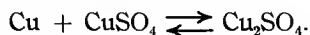
As a result of this fact, it is presumable that the corrosion will be increased by increasing the temperature, since more of the copper will dissolve in the cuprous form. Experiments were run at 95° in the electrolytes containing 75 grams per liter. The results of two runs are appended.

TABLE VII—COPPER

Run	Cathode coulometer	100 percent Cu	Time	C. D. amp/dm^2
1	0.6413	0.6413	1 hr.	3.0
2	0.558	0.558	1 hr.	2.6

Run		NaCl	Na$_2$SO$_4$	NaNO$_3$	NaC$_2$H$_3$O$_2$	Na$_2$C$_4$H$_4$O$_6$
1	g.	1.2959$_7$	0.6995$_8$	0.5321$_9$	0.4337$_4$	0.6595$_6$
	%	202.1	109.1	84.0	67.6	102.8
2	g.	1.1267$_4$	0.6423$_6$	0.4004$_8$	0.3741$_7$	0.5594$_9$
	%	201.9	115.1	71.7	67.0	100.2

The corrosion in the chloride solution was not increased by increasing the temperature. In the sulphate solution, very little if any increase was noted. In the tartrate solution, the increase was about 35 percent. The anodes in these solutions were fairly clean. On the other hand, the anode in the acetate solution was covered with a heavy adherent chocolate-brown oxide. The anode in the nitrate solution was covered with a nearly black oxide and, moreover, was deeply pitted and the depressions were filled with red cuprous oxide. As a result, the corrosion in the acetate solution while greater than at ordinary temperatures was not as great as expected. The corrosion in the nitrate solution was very much less than at ordinary temperatures, and part of this decrease is due to the adhering oxide and to the oxide included in the pits. When the adhering oxide was dissolved in a dilute mixture of sodium

chloride and hydrochloric acid and the anode dried and weighed, the corrosion was found to be:

	$NaC_2H_4O_2$	$NaNO_3$
Run 1	119.6	132.0
Run 2	128.4	161.0

However, as the results stand, the influence of temperature is disappointingly small.

When electrolyzing the tartrate solution with copper anodes, it was noticed that oftentimes a greenish yellow suspension was formed instead of a clear blue solution. When the suspension was allowed to settle, it was found that the supernatant liquid was blue, while at the bottom there settled out an orange-yellow precipitate which proved to be cuprous hydroxide. It was thought at first that this came from sodium chloride in the reagents or from the spattering of sodium chloride on the connectors during previous runs. The reagents contained no sodium chloride and with new connectors the same results were obtained. It was also found that large sheet copper anodes seemed to favor the formation of the cuprous hydroxide. The explanation is simple and interesting. Luther[1] has shown that formic acid is formed by oxidation of the tartrate on electrolyzing Fehling's solution with an insoluble anode. The formic acid reduces the Fehling solution and cuprous hydroxide, one of the products of the reduction, is precipitated. It has been shown that in the tartrate solution there is a tendency for the anode to "go passive," *i. e.*, to act like a noble metal. If any copper anode does act like a "noble metal," the oxygen liberated will oxidize the sodium tartrate, formic acid will be formed, and cuprous hydroxide will be precipitated. If a sheet copper anode became "passive," its large surface would give more efficient oxidizing, and would account for the fact that cuprous hydroxide was formed more readily with the sheet than with the smaller rod electrodes. When a current of 0.3 ampere

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[1] Luther: Zeit. Elektrochemie, **8**, 645 (1902).

was passed through a sodium tartrate solution for 4 hours with a large platinum anode and a small platinum cathode and then some freshly precipitated cupric hydroxide was added, part of the hydroxide was reduced, forming the orange-yellow cuprous hydroxide. If another portion of the tartrate solution was electrolyzed with a small platinum anode and a large platinum cathode and the same current was passed through for the same length of time, no reduction of the added cupric hydroxide took place. This shows that the reduction was due to the formation of some reducing compound by oxidation at the anode. However, a high anode density favored the formation of cuprous hydroxide when Fehling's solution was oxidized electrolytically with platinum electrodes.

Influence of Surface

Attention has been called to the fact that the condition of the electrode surface is one of the most important, if not the most important factor, which influences the corrosion. Some idea of the variation noticed with different electrodes may be gained from the following table. The electrodes were sheet copper and about 50 cm² of surface was exposed to the action of the current. The electrolysis was run in sodium tartrate solutions at room temperature.

TABLE VIII—COPPER

Run	Cathode coulometer	100 percent Cu	Time	C. D. amp/dm²
1	0.4095	0.4095	1 hr.	0.69
2	0.3917	0.3917	1 hr.	0.66
3	0.455	0.455	1 hr.	0.77

Run	$Na_2C_4H_4O_6$				
1	g. 0.3064a	0.2314b	0.3111d	0.2752e	
	% 74.8	56.5	76.0	67.2	
2	g. 0.3408c	0.3021f	0.3094h	0.3065g	0.2907e
	% 87.00	77.1	77.0	78.2	74.2
3	g. 0.2488c	0.3564f	0.2761	0.3638g	0.3625e
	% 54.7	78.3	60.7	80.0	79.7

G. R. White

The resistance of the circuit was so greatly increased by the formation of the green slimy coating on the anode that the current was cut down about half during the runs.

The experiment was repeated with the rod electrodes in place of the sheet. The results are given in the following table:

TABLE IX—COPPER

Run	Cathode coulometer	100 percent Cu	Time	C. D. amp/dm^2
1	0.2725	0.2725	1 hr.	1.3
2	0.1533	0.1533	1 hr.	0.72
3	0.2698	0.2698	1 hr.	1.2
4	0.3964	0.3964	2 h. 30 m.	0.74

Run	$Na_2C_4H_4O_6$				
1	g. 0.1523$_3$	0.1498$_4$	0.1663$_2$	0.1588$_5$	0.1550$_1$
	% 55.9	55.0	61.0	56.9	56.9
2	g. 0.1134$_9$	0.1002$_4$	0.1151$_7$	0.1128$_6$	0.1191$_8$
	% 74.0	65.4	75.1	72.0	77.7
3	g. 0.1722$_3$	0.1639$_4$	0.1660$_2$	0.1657$_5$	0.1528$_1$
	% 65.0	62.2	63.0	62.8	57.9
4	g. 0.2451$_3$	0.2359$_4$	0.2283$_2$	0.2311$_5$	0.2346$_1$
	% 61.8	59.5	57.6	58.3	59.2

One experiment was run for two and a half hours to see if longer exposure to electrolysis affected the passivity of the electrode and increased the quantity of cuprous hydroxide formed. In this experiment, only one of the solutions showed any of the hydroxide. Other experiments, which were run for three and a half hours, showed that at times the hydroxide was formed while at other times it was not, again emphasizing the importance of the electrode surface on the nature of the products formed by the electrolysis. In every case, if copper dissolved and did not go passive, no cuprous hydroxide was formed.

In the next group of experiments, copper was deposited on the copper rod electrodes from a coulometer solution and then corrosion experiments were run with the copper thus deposited. By using a proper current density, it is presumable

that the copper deposit will be uniform throughout and there-
fore the factor due to inhomogeneity should have been elim-
inated. If the deposit was not bright and free from streaks,
the electrode was not used. Experiments were conducted
at room temperature with sodium tartrate as the electrolyte.
In the first run, the percentage corrosion is not given. A
small current, 0.09 ampere, was used.

TABLE X—COPPER

Run	Time	C. D. amp/dm^2
I	I hr.	0.42

Run	Electrode	Na$_2$C$_4$H$_4$O$_6$			
I	g. 0.0888$_3$	0.0905$_1$	0.0875$_2$	0.0884$_5$	0.0835$_{10}$

Cuprous hydroxide was formed in every case and the results
are far from being uniform. One experiment was run with
the coulometer in series. The results follow:

TABLE XI—COPPER

Run	Cathode coulometer	100 percent Cu	Time	C. D. amp/dm^2
I	0.065	0.065	3 hr.	0.1

Run	Na$_2$C$_4$H$_4$O$_6$				
I	g. 0.0389$_3$ % 59.8	0.0393$_1$ 60.5	0.0394$_2$ 60.6	0.0364$_5$ 56.00	0.0362$_{10}$ 55.7

It was thought that the lack of uniformity in the results
might have been due to the fact that the surface of the anode
in the tartrate solution was slightly discolored and also to the
fact that at the surface of the electrolyte there was formed a
hard ring of bluish green precipitate which might not have
been removed completely. Sodium chloride solutions give a
very clean anode and therefore some experiments were tried

using it as the electrolyte. The copper was again deposited on the rods from the coulometer solution. In all these cases, more copper was deposited than dissolved off. The results are as follows:

TABLE XII—COPPER

Run	Cathode coulometer	100 percent Cu	Time	C. D. amp/dm$_2$
1	0.2014	0.2014	1 hr.	0.94
2	0.1437	0.1437	1 hr.	0.67

Run	NaCl				
1	g. 0.4061$_1$	0.4064$_2$	0.4066$_3$	0.4066$_5$	0.4062$_{10}$
	% 201.6	201.8	201.9	201.9	201.7
2	g. 0.2893$_1$	0.2896$_2$	0.2893$_3$	0.2907$_5$	0.2905$_{10}$
	% 201.3	201.5	201.3	202.3	202.1

The results in run 1 are very satisfactory while those in run 2 show discrepancies.

The results obtained with freshly deposited copper are not much more satisfactory than the results obtained with copper with no other precaution than filing the surface. This is shown in the following table.

TABLE XIII—COPPER
Electrodes filed

Run	Cathode coulometer	100 percent Cu	Time	C. D. amp/dm^2
1	0.2628	0.2628	1 hr.	1.22
2	0.2864	0.2864	1 hr.	1.33
3	0.2946	0.2946	1 hr.	1.37

Run	NaCl				
1	g. 0.5322$_4$	0.5308$_6$	0.5306$_7$	0.5210$_8$	0.5326$_9$
	% 202.5	202.0	202.9	198.3	202.7
2	g. 0.580$_4$	0.5720$_6$		0.5742$_8$	0.5642$_9$
	% 202.5	199.7		200.5	197.0
3	g. 0.5934$_4$	0.5936$_6$	0.5944$_7$	0.5878$_8$	0.5944$_9$
	% 201.4	201.5	201.8	199.5	201.8

These results seem to show that apparently a uniform surface cannot be obtained by deposition from coulometer solution or else the surface is not as important a factor as expected. The anodes which were prepared by filing were less discolored after the electrolysis than those upon which copper had been deposited.

In the electrolysis of nitrate solutions, nitrite was found in all cases. The presence of the nitrite might aid in the formation of the cuprous salts at the anode. Therefore, experiments were tried to see if the corrosion in sodium nitrite solutions (75 grams per liter) was greater than in nitrate. At the same time, the corrosion in ammonium nitrate solution was also studied. Since copper salts form soluble compounds with ammonium salts, it would be expected that the corrosion would be somewhat higher than with sodium nitrate because the surface of the anode would be kept cleaner. Such was not the case as the results show. One electrode was run in sodium nitrate for comparison.

TABLE XIV—COPPER

Run	Cathode coulometer	100 percent Cu	Time	C. D. amp/dm^2
1	0.6443	0.6443	1 hr.	3.0
2	0.480	0.480	1 hr.	2.2

Run	NaNO$_3$	NH$_4$NO$_3$	NaNO$_2$
1	g. 0.7656$_1$ % 118.8	0.6709$_2$ 104.1	0.7928$_6$ 123.1 0.7980$_7$ 123.9 0.8089$_9$ 125.6
2		g. 0.4955$_7$ % 103.3	0.5835$_1$ 121.8 0.5782$_2$ 120.5 0.5593$_6$ 116.5 0.5820$_9$ 121.2

In the sodium nitrite solution, the anode was coated with blue hydroxide which adhered strongly. Nearer the electrode surface the coating had a very pronounced green color. A greenish black precipitate was formed, the filtered supernatant liquid was alkaline and the odor of ammonia was detected. With ammonium nitrate, the anode was coated with a bluish green hydroxide and under this a very adherent brown oxide coating was formed. A blue solution containing a small amount of blue precipitate resulted. The results show that the corrosion in the sodium nitrite solution was greater than in sodium nitrate, while in the ammonium nitrate it was less than in sodium nitrate.

In sodium chloride, copper dissolves in the cuprous form. Experiments were tried to see how the copper dissolves in sodium bromide and iodide. One anode was run in sodium chloride for comparison. The results are given below.

TABLE XV

Run	Cathode coulometer	100 percent Cu	Time	C. D. amp/dm^2
1	0.4314	0.4314	1 hr.	2
2	0.9307	0.9307	2 hr.	2.2

Run	NaCl	NaBr	NaI
1	g. 0.8115$_3$ % 183.8	0.5385$_7$ 124.8 0.5479$_{10}$ 127.0	0.1287$_1$ 29.8 0.2283$_2$ 52.9
2	g. 1.8028$_4$ % 193.7	1.1628$_2$ 124.9 1.1284$_7$ 121.2	0.3215$_3$ 34.5 0.2616$_{10}$ 28.1

In the bromide solution, the anode was coated with a non-adherent hydroxide film and after this had been removed the surface was clean and bright. The precipitate was a mixture

of cuprous and cupric hydroxides. In the iodide solution, the anode was covered with a black adherent layer of iodine and under this some cuprous oxide was found. No precipitate was formed but the solution became yellow from the dissolved iodine. In both cases, the copper dissolved in part at least in the cuprous form. In neither case, was the corrosion as high as in the chloride solution. With the iodide, the small corrosion was due to the protecting action of the iodine on the anode.

Nickel

More work has been done on the behavior of nickel as anode than on any other metal except iron. In nickel plating baths, it is necessary that the anode shall dissolve as efficiently as possible and this, doubtless, accounts for the widespread interest in the anodic behavior of nickel. Saint Edmé[1] has shown that nickel becomes passive on immersion in ordinary nitric acid while iron requires immersion in fuming nitric before it becomes passive. He has also shown that nickel does not lose its passivity on passing chemically pure hydrogen over the red hot passive nickel for 7 or 8 hours and that ammonia is formed by the reaction. On the other hand, under these same conditions, iron loses its passivity. Pfanhauser[2] in his book on electroplating brought out the fact that in the plating bath nickel does not dissolve quantitatively according to Faraday's law and also that the amount of nickel which dissolved depended on whether the nickel anodes were rolled or cast. The question as to the influence which the nature of the anode has on the efficiency of corrosion was studied by Brown[3] who used nickel ammonium sulphate (75 grams per liter) for the electrolyte. The electrolysis was carried on at room temperature using 0.45 amp. hour and a current density of 4.12 amp. per sq. foot in each experiment. The results, taken from Table II in his paper, are as follows:

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[1] Saint Edmé: Comptes rendus, **106,** 1079 (1888).

[2] Pfanhauser: Electroplattierungen, 367 (1900).

[3] Brown: Trans. Am. Electrochem. Soc., **4,** 81 (1903).

Nickel anode	Current efficiency of corrosion Percent
Cast, surface ground smooth	46.3
Cast, surface roughened in acid	92.1
Rolled, pure	8.5
Electrolytic	12.6

These results show very plainly the influence of the nature of the anode on the efficiency. The general behavior of nickel anodes has been studied very carefully by LeBlanc and Levi,[1] Schoch[2] and Byers.[3]

The corrosion experiments with nickel were run in the same manner as the other metals. The anodes were made from nickel rods which contained only traces of iron, cobalt and carbon. The results with the larger current were as follows: In the chloride solution, the anode was slightly pitted ("speckled") and somewhat darkened. The precipitate was apple-green nickelous hydroxide. In the sulphate solution, the anode was smooth and coated with a thin light brown film of oxide. The precipitate was a dirty green with black specks of nickelic oxide scattered through. In the nitrate solution, the anode was smooth and slightly tarnished; at the surface of the electrolyte, a black non-adherent ring of nickelic oxide was formed. The appearance of the precipitate was about the same as in sulphate solution except that it contained more black specks of the nickelic oxide. In both sulphate and nitrate solutions, some brown gelatinuous precipitate of the nickelic hydroxide was formed in small quantities by oxidation of the nickelous hydroxide. The anodes in sodium acetate and tartrate were unaffected and no precipitate was formed. In this connection, it is interesting to note that in the nickel plating bath unless some compound is added which can dissolve nickel oxide, it will

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[1] LeBlanc and Levi: Loc. cit.

[2] Schoch: Loc. cit.

[3] Byers: Loc. cit.

be formed on the anode.[1]   No metal was deposited on the nickel wire cathode in any of the experiments and the filtered electrolyte was alkaline in all cases.

The numerical results with the larger current at room temperature are given in the following table.

Table XVI—Nickel
At. wt. 58.7; equivalent weight, 29.35
Average anode surface, 10.3 cm^2

Run	Cathode coulometer	100 percent Ni	Time	C. D. amp/dm^2
1	0.319	0.3867	1 hr.	3.4
2	0.4611	0.4256	1 hr.	3.8
3	0.5549	0.5121	1 hr.	4.5
4	0.5898	0.5444	1 hr.	4.8
5	1.2138	1.1171	2 hr.	5.0
6	0.9444	0.8716	1 h. 30 m.	5.2

Run	NaCl	Na$_2$SO$_4$	NaNO$_3$	NaC$_2$H$_3$O$_2$	Na$_2$C$_4$H$_4$O$_6$
1	g. 0.3914$_6$	0.0078$_4$	0.0122$_3$	0.0066$_1$	0.0069$_2$
	% 101.2	2.0	3.1	1.7	1.8
2	g. 0.4368$_1$	0.0136$_2$	0.020$_3$	0.0024$_5$	0.0122$_4$
	% 102.6	3.2	4.7	0.6	2.9
3	g. 0.5280$_6$	0.0093$_4$	0.0148$_3$	0.0031$_1$	0.0120$_2$
	% 103.1	1.8	2.9	0.6	2.3
4	g. 0.5765$_{11}$	0.0160$_8$	0.0105$_7$	0.0020$_{10}$	0.0095$_9$
	% 105.9	2.9	1.9	0.4	1.7
5	g. 1.1404$_{12}$	0.0157$_8$	0.0286$_{10}$		0.0189$_7$
	% 102.1	1.4	2.6		1.7
			0.0297$_{11}$		
			2.7		
6	g. 0.8837$_{10}$	0.0120$_8$	0.0258$_{11}$	0.0137$_{13}$	0.0198$_7$
	% 101.4	1.4	3.0	1.6	2.3

The results showed that nickel is very little affected by any of the electrolytes except the chloride.   It was noticed that a new anode, which was cleaned by scouring with carborundum paper and rinsing in distilled water and absolute alcohol, showed a greater corrosion the first time it was made

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[1] Tommasi: Electrochimie, 258.

anode in an acetate solution than in any subsequent run. Since the chloride has such a marked effect, precautions were taken to use salts which were chloride free. The excess corrosion in the case of the chloride cannot be explained by the formation of a nickel salt in which the valence of the nickel is one because Denham[1] has shown by an experiment in which metallic nickel was heated with neutral nickel sulphate in the warm limb of the "circulation apparatus" of Richards, Collins and Heimrod that there was no tendency for the nickel to dissolve and to be precipitated in the cold limb. However, in this, as in some other cases, the anode was coated with a non-adherent powder which may be metal in a very fine state of division accounting for a part of the excess corrosion. The fact has already been brought out that the precipitate, as a rule, contains no metallic particles large enough to dissolve in hydrochloric acid with marked evolution of gas.

The fact that sodium chloride dissolves the nickel quantitatively accounts for the fact that platers usually add a handful of table salt to the plating bath. At one time there were on the market "exciting salts"[2] which were purported to increase the conductivity and to insure a bright adherent deposit. Sodium chloride was a constant ingredient in nearly all these "exciters."

If cast nickel, which contained iron and carbon in fairly large amounts but no copper or tin, was made anode in a solution of nickel ammonium sulphate (60 grams per liter) the average corrosion for three runs was 4.3 percent. The electrolysis was carried on for an hour at room temperature with a current density of 1.5 amperes per dm². If 0.15 gram of NH_4Cl was added to the above solution, the same anode showed an average corrosion of 94 percent for three runs when the electrolysis was conducted under the same temperature and current conditions as in the previous case. This ex-

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[1] Denham: Jour. Chem. Soc., **93**, 833 (1908).
[2] LeRoy: Rev. de chim. ind., **7**, 70 (1886).

periment shows how the efficiency is increased by the addition of a chloride.

If sheet nickel was made anode in a solution of nickel sulphate (40 grams per liter), the average corrosion for three runs was 3 percent for a run of an hour at room temperature with a current density of 3 amperes per sq. dcm. Snowdon[1] has shown that it is possible to plate nickel on nickel if the nickel cathode is first reduced by making it cathode in a 3 normal solution of hydrochloric acid using a current density of 8 amp. per dm² for four minutes. By this treatment the oxide film is reduced and the nickel can be made to adhere strongly. This suggested a treatment for the nickel anodes and experiments were run in which nickel was made cathode in 4 normal sulphuric acid and reduced for four minutes with a current of 8 amp. per dm². Then, after quickly rinsing in distilled water, it was transferred to a solution of nickel sulphate in which it was run as anode for 15 minutes. It was then rinsed with distilled water and made cathode again for 5 minutes in the sulphuric acid. This treatment was repeated until the nickel had been run as anode for an hour. By this treatment the corrosion was increased from 3 to 12 percent. The experiment was conducted at room temperature and the current was determined by taking readings every minute during the time the nickel was acting as anode. The increased corrosion cannot be explained by loss of nickel by solution in the sulphuric acid because experiments showed that the amount of nickel thus dissolved when it was cathode in the acid was only about 0.002 gram an hour. Apparently, during electrolysis in the sulphate solution, the anode underwent some change which caused it to corrode poorly, *i. e.*, "to go passive" and this tendency was overcome, in part, by subjecting the anode to the action of hydrogen from time to time and was overcome almost entirely by the addition of a chloride to the sulphate solution.

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[1] Snowdon: Jour. Phys. Chem., **9**, 399 (1905).

Since nickel dissolves quantitatively in chloride solution and only slightly in the other electrolytes, the effect of adding known amounts of sodium chloride solution to the other solutions was tried. When 5 cc of the chloride solution was added to 195 cc of the sulphate solution, the corrosion was increased very markedly. The smallest corrosion noted with this mixed electrolyte of chloride and sulphate solutions was 9 percent; the largest was 100 percent. The average of twenty experiments was 65 percent—a very marked increase over the corrosion in the pure sulphate solution. With pure sulphate solution, the precipitate was green with some black specks of nickelic oxide scattered through and discolored by a gelatinous brown precipitate which is doubtless the nickelic hydroxide. With the "mixed electrolytes," the precipitate contained much more of the black oxide and the brown hydroxide and if the quantity of precipitate was small (*i. e.*, if the amount of corrosion was small), it was in most cases composed entirely of a mixture of the black oxide and brown hydroxide. These nickelic compounds were formed by the oxidizing action of the hypochlorite which was formed when the anode became passive and the chlorine, set free there, reacted with the alkali formed at the cathode. The addition of 5 cc of chloride solution to 195 cc of the acetate solution increases the corrosion from a fraction of a percent to the theoretical value with the precipitation of apple-green nickelous hydroxide. The same quantity of chloride solution added to the tartrate solution increased the corrosion from about 2 to 96 percent. The precipitate in this case also was apple-green. With sodium nitrate, it required the addition of a larger amount of the chloride to overcome the passivity of the nickel. With 5 cc of the chloride, the corrosion was only about 8 percent. It requires the addition of about 15 cc of the chloride to increase the corrosion up to theoretical. In all these cases, the amount of chloride required to make the anode corrode quantitatively varied with the electrode. The results given are the average of a number of experiments. The electrolysis was carried on at room temperature with a

current density of from 3–5 amperes per dm². In this group of experiments with the "mixed electrolytes," the tendency of the nickel to become passive was opposed and in some cases overcome by the addition of the chloride. Le-Blanc and Levi have shown that the passivity of nickel is also overcome by heating the electrolyte during electrolysis.

With the smaller current, the corrosion was greater in every case, excepting the chloride, than with the larger current. The appearance of the anodes and precipitates was about the same as with the larger current—at least there were no striking points of difference. The results with the lower current density are given in the next table.

TABLE XVII—NICKEL

Run	Cathode coulometer	100 percent Ni	Time	C. D. amp/dm²
1	0.4304	0.3972	8 hr.	0.28
2	0.2529	0.2334	6 hr.	0.34
3	0.2577	0.2378	6 hr.	0.35
4	0.2946	0.2719	6 h. 40 m.	0.36
5	0.303	0.2797	4 h. 40 m.	0.37

Run	NaCl	Na$_2$SO$_4$	NaN$_3$O	NaC$_2$H$_3$O$_2$	NaC$_4$H$_4$O$_6$
1	g. 0.4106$_5$ % 103.2	0.0524$_4$ 13.2	0.0324$_3$ 8.2	0.011$_1$ 2.8	0.0256$_2$ 6.4
2	g. 0.238$_7$ % 102.0	0.0486$_9$ 20.8	0.0253$_8$ 10.8	0.0026$_{11}$ 1.1	0.0194$_{10}$ 8.3
3	g. 0.2452$_1$ % 103.1	0.0542$_2$ 22.8	0.031$_3$ 13.0	0.0046$_5$ 1.9	0.015$_4$ 6.3
4	g. 0.2806$_1$ % 103.2	0.035$_2$ 12.9	0.0236$_3$ 8.7	0.003$_5$ 1.1	0.0138$_4$ 5.1
5	g. 0.2856$_5$ % 102.1	0.0452$_4$ 16.2	0.0308$_3$ 11.0	0.001$_1$ 0.4	0.0186$_2$ 6.6

For sake of comparison, the results obtained by LeBlanc and Levi[1] and Byers[2] are here included. The former workers

[1] LeBlanc and Levi: Loc. cit.

[2] Byers: Loc. cit.

used a 1.5 percent solution which was electrolyzed at room temperature. Their results are given in the following table:

Electrolyte	C. D. amp/dm²	Electrode loss Percent
NaCl	0.5	100.0
NaNO$_3$	0.5	5.0
Na$_2$SO$_4$	0.5	2.0
NaC$_2$H$_3$O$_2$	0.5	45.0
NaC$_2$H$_3$O$_2$	0.42	63.0
NaC$_2$H$_3$O$_2$	0.32	42.0

Byers gives the following results with electrolytic nickel on electrolysis at room temperature.

Electrolyte	C. D. amp/dm²	Electrode loss Percent
Na$_2$SO$_4$	0.4	74.8
Na$_2$SO$_4$	0.4	100.0
Na$_2$SO$_4$	0.5	2.0
NaC$_2$H$_3$O$_2$	0.5	3.4

These results are uniformly higher and in some cases strikingly higher than the results given in Table XVI.

Some experiments were also made with a very small current, *i. e.*, 3–4 milliamperes. The results show very little increase in corrosion over that noted with the other small current density. It was thought that with this small current the corrosion would be very nearly theoretical because the tendency to become passive was shown to be less the lower the current density. The electrolytes, of course, contained air in solution and this dissolved air may account for the continuance of a partially passive state. The results are given in the following table:

TABLE XVIII—NICKEL

Run	Cathode coulometer	100 percent Ni	Time	C. D. amp/dm²
1	0.0245	0.0226	10 hr.	0.02
2	0.0391	0.0361	10 hr.	0.03
3	0.0435	0.0382	10 hr.	· 0.036
4	0.0505	0.0444	10 hr.	0.04

Run	Na_2SO_4	$NaNO_3$	$NaC_2H_3O_2$	$Na_2C_4H_4O_6$
1	g. 0.0097₄ / % 42.9		0.0005₃ / 2.2	0.002₂ / 8.8
2	g. 0.0067₂ / % 18.6		0.0005₄ / 1.4	0.0027₂ / 7.5
3	g. 0.0120₄ / % 29.9	0.0073₂ / 18.6		0.0027₃ / 6.7
4	g. 0.0118₂ / % 25.3		0.0007₄ / 1.5	0.0027₃ / 5.8

The amounts of metal lost by corrosion were so small that the results are at best untrustworthy. The loss in the tartrate solution might be due to chemical corrosion since the same loss was obtained in three runs.

Some experiments were also tried with electrolytes containing 25 grams of salt per liter instead of the usual concentration, 75 grams. The corrosion was not greatly different from that in the more concentrated solution. The experiments were run at room temperature. The results are given in Table XIX.

Some runs were made, using ammonium salts as electrolytes in place of the sodium salts. The average results ran a little higher than with the sodium salts, except with the chloride solution. The general increase of the corrosion noted may be accounted for by the fact that the ammonium salts form soluble compounds with nickel hydroxide and this would tend to keep the anodes free from adhering hydroxide thus increasing the possibility of corrosion by removing any insoluble compound which might protect the anodes. The

G. R. White

TABLE XIX—NICKEL

Run	Cathode coulometer	100 percent Ni	Time	C. D. amp/dm^2
1	0.3675	0.3392	1 hr.	3.0
2	0.4418	0.4078	1 hr.	3.6

Run	Na$_2$SO$_4$	NaNO$_3$	NaC$_2$H$_3$O$_2$	Na$_2$C$_4$H$_4$O$_6$
1	g. 0.0081$_4$ % 2.4 g. 0.0106$_6$ % 3.1	0.0107$_1$ 3.1	0.0012$_3$ 0.3	0.0181$_2$ 5.3
2	g. 0.0098$_4$ % 2.4 g. 0.0131$_1$ % 3.2	0.0103$_6$ 2.5	0.0012$_2$ 0.3	0.0098$_3$ 2.4

anodes, as a matter of fact, were always much cleaner than with the sodium salts. No precipitate was formed in any of the solutions and after electrolysis the filtered electrolyte was alkaline. The chloride became a blue color, the sulphate and sometimes the nitrate, a very faint green, the tartrate a yellow-brown color which was due to the oxidizing action of the oxygen liberated at the anode on the tartrate solution. The same color was obtained when the tartrate solution was electrolyzed with a large platinum anode. The electrolysis was run at room temperature with the larger current. The results are given in the following table:

TABLE XX—NICKEL

Run	Cathode coulometer	100 percent Ni	Time	C. D. amp/dm^2
1	0.470	0.4337	1 hr.	3.8
2	0.4806	0.443	1 hr.	3.9
3	0.5349	0.4937	1 hr.	4.4
4	0.6184	0.5708	1 h. 20 m.	3.6
5	0.6989	0.6451	1 h. 15 m.	4.8

Run	NH_4Cl	$(NH_4)_2SO_4$	NH_4NO_3	$NH_4C_2H_3O_2$	$(NH_4)_2C_4H_4O_6$
1	g. 0.4338_7 % 100.0	0.0618_9 11.3	0.0404_8 9.3	0.0083_{12} 1.9	0.0139_{10} 3.2
2	g. 0.4445_9 % 100.3	0.0344_8 7.8	0.0154_7 3.5	0.0037_{10} 0.8	0.0313_{12} 7.1
3	g. 0.4996_{12} % 101.2	0.0535_8 10.8	0.0228_9 4.6	0.0049_7 1.0	0.0153_{10} 3.1
4	g. 0.5786_9 % 101.9	0.1321_{12} 23.1	0.0172_7 3.0	0.0109_8 1.9	0.0750_{11} 13.1
5	g. 0.6473_8 % 100.3	0.0353_7 5.5	0.0407_{12} 6.3	0.0081_9 1.2	0.0218_{10} 3.4

In sodium chloride, nickel corroded quantitatively. Some experiments were conducted to see what efficiency sodium bromide and iodide (75 grams per liter) would give. The bromide gave about as high an efficiency as the chloride. The precipitate was the apple-green hydroxide and the anode was clean and not greatly discolored. The filtered supernatant liquid was alkaline to litmus. The iodide gave a very much lower efficiency and a large amount of iodine was set free at the anode. The precipitate was colored a deep brown by the iodine. In order to see what the color of the precipitate was, the iodine was dissolved by alcohol. By frequent washing, all the alcohol could be removed and the precipitate was found to be apple-green. During the washing process, the odor of aldehyde was noticed and it was thought that any nickelic compound which might be present might have oxidized the alcohol. It was found later that black nickelic oxide did give the odor of aldehyde when treated with alcohol and that, by long-continued washing, it could be reduced to the green nickelous hydroxide. The results on electrolyzing with the larger current at room temperature are given in the next table.

TABLE XXI—NICKEL.

Run	Cathode coulometer	100 percent Ni	Time	C. D. amp/dm^2
1	0.325	0.2999	1 hr.	2.7
2	0.3768	0.3477	1 hr.	3.1
3	0.4382	0.4043	1 hr.	3.5
4	0.442	0.408	1 hr.	3.6
5	0.4543	0.4193	1 hr.	3.7

G. R. White

TABLE XXI—(*Continued*)

Run	NaI	NaBr
1	g. 0.1474_{15}	0.3033
	% 49.1	101.16
	g. 0.1164_{18}	0.3054
	% 38.8	101.85
	g. 0.1615_{17}	
	% 53.8	
2	g. 0.148_{12}	0.352_{10}
	% 42.6	101.2
	g. 0.1525_{11}	
	% 43.8	
	g. 0.1458_{3}	
	% 41.9	
	g. 0.1543_{6}	
	% 44.4	
3	g. 0.4048_{3}	precipitate green
	% 100.1	
	g. 0.1673_{6}	
	% 41.4	
	g. 0.4305_{4}	precipitate green
	% 106.5	
	g. 0.4309_{2}	precipitate green
	% 106.6	
	g. 0.0575	
	% 14.2	
4	g. 0.1816_{6}	0.4094_{2}
	% 44.6	100.4
	g. 0.4457_{3}	0.4082_{1}
	% 109.3	100.0
		0.4102_{4}
		100.5
5	g. 0.1447_{14}	
	% 34.5	
	g. 0.1585_{1}	
	% 37.8	
	g. 0.0808_{19}	
	% 18.8	
	g. 0.0467_{8}	
	% 11.1	
	g. 0.1738_{20}	
	% 41.4	

The corrosion with the iodide solution showed great fluctuation—again indicating the importance of the surface as a factor

in determining the amount of corrosion. Whenever the corrosion was the theoretical value, the precipitate was green.

For sake of comparison, the corrosion in potassium iodide and bromide solutions as determined by LeBlanc and Levi are given. The 1.5 percent solution was electrolyzed at room temperature.

Electrolyte	C. D. amp/dm²	Electrode loss Percent
KI	0.5	101
KBr	0.5	102

This current density was lower than that used in the above experiments.

Tin

The corrosion of tin was studied under the same conditions as the other metals. The anodes were made from "tin sticks" which were free from lead and copper but contained a trace of iron. In every case, the analyses of all the anode metals were made by following the methods given in Krauch, "The Testing of Chemical Reagents for Purity." The appearance of the anodes after electrolysis was very characteristic. In the chloride solution, the anode was very badly pitted and a deep irregular ring was always gouged out at the surface of the electrolyte. The anode was coated with a black film, most of which came off on cleaning, leaving the surface fairly clean. Despite the pitting—or gouging would perhaps more nearly describe the phenomenon—the amount of metal found in the precipitate was very small. In the sulphate solution, the anode was covered with a light brown oxide which was difficult to remove and which discolored the surface. On drying, it was possible to remove much of the oxide by scraping with the finger nail. The wide discrepancies in the results with the sulphate solution are due, in some measure at least, to the adherence or non-adherence of this oxide to the anode. In the nitrate solution, a heavy grayish brown hydroxide was formed which could be removed by

rubbing energetically, leaving a clean anode surface. In most of the runs this hydroxide layer was 2 mm thick. It was soluble in hydrochloric acid without evolution of gas. In the acetate solution, the anode had a brown and white mottled appearance due to the mixture of the two hydroxides which formed on the anode. They could be removed almost completely, leaving the anode spotted brown and white. In the tartrate solution, a glistening dark brown or black oxide was formed which caused a very marked increase in the resistance of the circuit. Part of this oxide rubbed off but the greater part adhered strongly. In describing the compound which adhered to the anode, the terms oxide and hydroxide are used indiscriminately because no attempt was made to ascertain definitely whether they were hydroxides or hydrated oxides. In all the solutions, except the tartrate, a precipitate was formed which was a mixture of white and brown, the latter indicating that some of the tin dissolves in the tetravalent form. In the nitrate solution, the precipitate had a decided gray tinge and the oxide which adhered to the anode was a more pronounced gray than the precipitate. In regard to this gray-colored compound, Tommasi[1] called attention to the fact that when tin was fused in air, a gray coating was formed on the metal which was a mixture of stannous and stannic oxides. Furthermore, Fuchs[2] has shown that if stannous chloride is added to ferric chloride until the latter loses its color and becomes slightly green and then calcium carbonate is added to the above mixture with gentle heating, a precipitate is formed which he called tin sesquioxide. He described it as a grayish white, slimy solid having the composition Sn_2O_3. This is now believed to be a mixture of stannous and stannic oxides (SnO and SnO_2).

Some metal was deposited at the cathode in all the solutions except the tartrate. The filtered supernatant liquid was alkaline in all cases but not alkaline enough to dissolve a suffi-

[1] Tommasi: Electrochimie, 313.
[2] Fuchs: Jour. prakt. Chemie, 5, 318 (1835).

cient amount of the metal to account for any large excess corrosion.

The numerical results on electrolyzing at room temperature with the larger current are given in the next table.

TABLE XXII

At. wt. 119; equivalent weight, 59.5
Average anode surface, 15.8 cm^2

Run	Cathode coulometer	100 percent Sn	Time	C. D. amp/dm^2
1	0.3366	0.6298	1 hr.	1.8
2	0.4324	0.8095	1 hr.	2.3
3	0.6994	1.3088	1 hr.	3.7
4	0.5832	1.0912	1 hr.	3.1
5	0.4006	0.7496	1 hr.	2.1
6	0.3527	0.6599	1 hr.	1.9
7	0.4462	0.8349	1 hr.	2.4

Run	NaCl	Na$_2$SO$_4$	NaNO$_3$	NaC$_2$H$_3$O$_2$	Na$_2$C$_4$H$_4$O$_6$
1	g. 0.6396$_5$	0.2668$_1$	1.2036$_2$	0.5796$_3$	0.060$_4$
	% 101.6	42.4	191.1	92.0	9.5
2	g. 0.8128$_5$	0.0470$_1$	1.5498$_2$	0.3454$_3$	0.0576$_4$
	% 100.5	5.8	191.6	42.7	7.1
3	g.	0.3768$_1$	2.2614$_4$	0.947$_3$	0.1100$_2$
	%	28.8	172.8	72.4	8.4
			2.38$_6$		
			181.9		
4	g. 1.1002$_6$	0.3008$_1$	2.0748$_2$	0.9264$_3$	0.0742$_4$
	% 100.8	27.6	190.1	84.9	6.8
5	g. 0.7622$_8$	0.6321$_9$	1.4027$_1$	0.6642$_{10}$	0.0552$_{12}$
	% 101.7	84.3	187.1	88.6	7.4
6	g. 0.6289$_4$	0.2290$_6$	1.2075$_8$	0.562$_{12}$	0.0473$_9$
	% 95.3	34.7	183.6	85.2	7.2
7	g. 0.7147$_7$	0.6025$_2$	1.344$_5$	0.7576$_3$	0.0327$_4$
	% 85.6	72.2	161.0	90.7	3.9

The results show wide discrepancies in some cases and no definite explanation can at present be offered for the lack of uniformity.

An experiment was tried in which five tin anodes were run in series at room temperature with sodium sulphate as

electrolyte. The anodes had been used in several runs al-
though they were filed before this run according to the usual
procedure. The corrosion showed a variation of about 7
percent and was much less than the highest efficiency of
corrosion noted. The results are given below.

Run	Cathode coulometer	100 percent Sn	Time	C. D. amp/dm^2
I	0.3596	0.6729	I hr.	1.9

Run	Na$_2$SO$_4$				
I	g. 0.2012$_1$ % 29.9	0.1880$_2$ 27.9	0.1896$_4$ 28.2	0.210$_5$ 31.2	0.2386$_6$ 35.5

Some of the tin which was used for anodes was found to
be honey-combed with "blow holes" some of which were very
large. Therefore, it was thought worth while to cast some tin
and to use these newly cast sticks for anodes with the hope
that these "blow holes" could be obviated by careful casting.
Granulated tin (C. P.) was fused in a graphite crucible and
cast into sticks (8 cm long × 0.8 cm diam.) in a graphite
mould. These sticks were free from "blow holes" but the
results obtained on electrolysis at room temperature failed to
show uniform corrosion as the following table shows.

TABLE XXIII—TIN (newly cast)

Run	Cathode coulometer	100 percent Sn	Time	C. D. amp/dm^2
I	0.5026	0.9404	I hr.	2.7
2	0.4557	0.8527	I hr.	2.4

Run	NaCl	Na$_2$SO$_4$	NaNO$_3$	NaC$_2$H$_3$O$_2$	Na$_2$C$_4$H$_4$O$_6$
I	g. 0.8008$_a$ % 85.2	0.6645$_c$ 72.3	1.5037$_b$ 159.9	0.869 $_e$ 92.4	0.0477$_d$ 5.1
2	g. 0.7818$_f$ % 91.7	50.81$_c$ 59.6	1.3728$_b$ 161.0	0.6561^e 75.4	0.0024$_d$ 0.3

The results in the chloride and nitrate solutions ran quite a little lower than the average in the other runs. In the sulphate solution, the corrosion was much higher than it was when the five anodes were run in series and approached the higher values. In the second run, the anode became passive in the tartrate solution. In the acetate solution, the results were about the same.

The corrosion of tin in sodium chloride and sulphate solutions has been studied by Elbs and Thümmel.[1] They used solutions of two concentrations and three different current densities. After electrolysis, the solution was neutral which showed that the hydroxide and not a basic salt was precipitated. The anode was wrapped in cotton cloth to prevent the loss of pieces which fall from the electrode. Their results showed that only about 10 percent of the tin dissolved in the tetravalent form while 90 percent dissolved in the divalent form. Part of their results are here given. The temperature throughout was 18°.

Electrolyte	Concentration Grams per liter	C. D. amp/dm²	Corrosion efficiency Percent
NaCl	117	1.0	98.8
NaCl	117	10.0	99.8
NaCl	5.85	1.0	90.8
NaCl	5.85	10.0	96.5
Na_2SO_4	142	1.0	93.0
Na_2SO_4	142	10.0	94.2
Na_2SO_4	7.1	1.0	95.5
Na_2SO_4	7.1	10.0	94.4

The most striking point in Table XXII is the high corrosion efficiency in the nitrate solution. As stated before, this excess corrosion was not due to mechanical disintegration because the precipitate and adhering oxide dissolved in hydrochloric acid without evolution of gas. The average corrosion was well above 175 percent when the assumption was made

[1] Elbs and Thümmel: Zeit. Electrochemie, 10, 365 (1904).

that all the tin dissolves in the divalent form. Some of the metal dissolved in the tetravalent form, as Elbs and Thümmel have shown, but this would tend to make the results lower rather than higher because the equivalent weight of tetravalent tin is 29.75 while that of divalent tin is 59.5. There is a possibility that some of the tin dissolved in the monovalent form. In the literature, no reference could be found to the existence of any oxide of tin having the formula Sn_2O. However, lead, another metal in the fourth group of the periodic table which is most closely analogous to tin— also a member of this group—forms a suboxide Pb_2O. According to Berzelius, the gray oxide which is formed on the surface of lead when it is exposed to air consists of Pb_2O. Dulong showed that a black powder remained, after the residue had cooled in the retort, when lead oxalate was heated to 300° out of contact with the air until no more gas was given off. When heated in air, this black powder burned to lead oxide. When heated out of contact with the air, it gave lead oxide and metallic lead. When moist, it absorbed oxygen from the air and formed a hydrated lead oxide, $PbO.xH_2O$. On treating the suboxide with dilute acids or with a saturated solution of lead nitrate, it was transformed into lead oxide. It is not a mixture of lead oxide and metallic lead because, when rubbed with mercury either dry or under water, no lead was removed. Furthermore, lead oxide was not removed by boiling with lead acetate. Tanatar[1] has shown that it can also be prepared when lead oxalate is heated in a combustion tube to the lowest possible temperature necessary to decompose the oxalate and a stream of dry carbon dioxide is conducted through the apparatus. He described the substance as a grayish black powder which can be decomposed in the cold when treated with a 10 percent solution of sodium hydroxide which dissolves the oxide and leaves the metallic lead. The specific gravity of this suboxide was different from that of a mixture of lead oxide and metallic lead. Tanatar also

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[1] Tanatar: Zeit. anorg. Chem., **27**, 304 (1901).

measured the heat evolved when a gram molecule of this compound was dissolved in acetic acid and compared the value thus obtained with Thomsen's value for the heat evolved when lead oxide dissolves in acetic acid. The two values were not the same which is another indication that this is a definite compound. Denham[1] has shown that lead, when heated with lead acetate in the warm limb of the circulation apparatus, is deposited in the cold arm, indicating a reaction which takes place as follows: $Pb + PbC_2H_3O_2 = Pb_2C_2H_3O_2$ and which is a further indication of monovalent lead.

When lead was made anode in a solution of sodium nitrate and the solution was electrolyzed at room temperature, a white precipitate was formed and at the anode a dark gray oxide which could be easily removed leaving the surface clean. The filtered supernatant liquid was alkaline and a spongy deposit of lead was formed at the cathode. The solution also contained large quantities of nitrite. The results are given below.

TABLE XXIV—LEAD

At. wt. 207.1; equivalent weight, 103.55
Average anode surface, 12.5 cm^2

Run	Cathode coulometer	100 percent Pb	Time	C. D. amp/dm^2	NaNO$_3$
1	0.5357	1.7104	1 hr.	3.6	g. 1.8003 % 102.8
2	0.5407	1.7607	1 hr.	3.6	g. 1.8377 % 104.4

The results are very much lower than required to indicate that some of the lead had dissolved in the monovalent form.

The results for the corrosion of tin with the lower current density are as follows. The electrolysis was carried on at room temperature.

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[1] Denham: Loc. cit.

TABLE XXV—TIN

Runs	Cathode coulometer	100 percent Sn	Time	C. D. amp/dm^2
1	0.1086	0.2032	5 hrs.	0.12
2	0.1062	0.1978	5 hrs.	0.12
3	0.107	0.2003	5 hrs.	0.12

Run	NaCl	Na$_2$SO$_4$	NaNO$_3$	NaC$_2$H$_3$O$_2$	NaC$_4$H$_4$O$_6$
1	g. 0.1874$_5$	0.1378$_3$	0.2686$_4$	0.0790$_1$	0.0026$_2$
	% 92.2	67.8	132.2	38.9	1.3
2	g. 0.145$_5$	0.0398$_3$	0.2834$_4$	0.0724$_1$	0.001$_2$
	% 73.3	20.1	143.3	36.6	0.5
3	g. 0.187$_3$	0.0952$_5$	0.280$_2$	0.0628$_1$	0.0064$_4$
	% 93.4	47.6	139.8	31.4	3.3

In the chloride solution, the corrosion was about the same as with the higher current density. In the sulphate solution, it was somewhat less than in the other case. In the nitrate, acetate and tartrate solutions, it was quite appreciably less. The appearance of the anodes was about the same in both cases and the filtered supernatant liquid was alkaline. Metal was deposited in all solutions in which it was formed with the larger current.

Curry[1] has shown that the corrosion of bronzes increased very rapidly as the tin content increased. In solutions of sodium sulphate, acetate and alkaline tartrate, the tin-rich bronzes corroded very readily but with increasing amounts of the E phase the corrosion showed a marked decrease. With increasing amounts of pure tin in the bronze, the corrosion was found to increase. In sodium nitrate solution, the corrosion was very much higher than the theoretical, especially as the tin content increased. With pure tin, the corrosion was about 2.5 times the corrosion in the coulometer when the assumption was made that all the tin dissolved in the tetra-valent form. The fact that tin corroded readily in sulphate,

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[1] Curry: Jour. Phys. Chem., **10**, 482 (1906).

chloride and nitrate solutions was also mentioned in this paper. In this work, the electrolysis was carried on at room temperature for 8 hours with a current of 0.025 ampere. The current density was 0.18 amp/dm^2.

In the sodium nitrate solution, nitrite was formed by reduction as usual. It was thought that the nitrite might increase the corrosion of the tin. Therefore, some experiments were tried with a solution of sodium nitrite (75 grams per liter). Some experiments were also tried with a solution of ammonium nitrate of the same concentration to see how another nitrate affected the tin. The results with the larger current on electrolyzing at room temperature are given in the following table. In the first run, one test was made with sodium nitrate for comparison.

TABLE XXVI—TIN

Run	Cathode coulometer	100 percent Sn	Time	C. D. amp/dm^2
1	0.5375	1.0067	1 hr.	2.8
2	0.4727	0.8845	1 hr.	2.5
3	0.4483	0.8388	1 hr.	2.4

Run	NaNO$_3$	NaNO$_2$	NH$_4$NO$_3$
1	g. 1.6791$_4$ % 167.0	0.1137$_5$ 11.3	1.6449$_2$ 163.6 1.8875$_6$ 187.7
2		0.0105$_5$ 1.2 0.1479$_7$ 16.7	1.4910$_4$ 168.6 1.4519$_2$ 164.2 1.6515$_6$ 186.7
3		0.085$_5$ 10.1 0.0987$_6$ 11.8	1.5446$_5$ 184.1 1.3666$_2$ 162.9 1.3248$_7$ 157.9

In the nitrite solution, only a small amount of the gray-colored precipitate was formed. The anode was covered with a dark adherent oxide and the solution was alkaline to litmus. The corrosion was small and the action of the nitrite formed will not explain the excess corrosion in the nitrate solution. In the ammonium nitrate solution, a heavy white precipitate was formed. The anode was covered by a grayish brown oxide which could be readily removed, leaving a fairly clean surface. In this case also, the filtered supernatant liquid was alkaline to litmus and the odor of ammonia was plainly noted.

Iron

From the time of Keir[1] who discovered that iron when immersed in nitric acid (sp. gr. 1.45) did not dissolve, up to the present time, the passivity of iron has interested chemists. Various explanations have been offered for this phenomenon, ranging from the "oxide film" theory of Faraday and Schönbein[2] to the "velocity of reaction between metal and anodic oxygen" theory of Fredenhagen.[3] Recently Krassa[4] has come forward with experiments from which he concludes that the passivity is due to a "skin of oxide." This conclusion completes a cycle of explanation and theory has again arrived at the first explanation given for passivity, namely, the "oxide film" theory. A very complete bibliography of this subject is given by Heathcote[5] and DeBenneville[6] gives a critical survey of the field up to the time his paper was published.

Assuming that an oxide film was formed, attempts have been made to determine its thickness by a study of its power to reflect polarized light. Micheli[7] showed that this method indicated that the optical properties of the surface

[1] Keir: Phil. Trans., 80, 359 (1790).

[2] Faraday: Expt. researches, 2, 231.

[3] Fredenhagen: Zeit. phys. Chem., 63, 1 (1908).

[4] Zeit. Elektrochemie, 15, 490 (1909).

[5] Heathcote: Loc. cit.

[6] DeBenneville: Jour. Iron and Steel Inst., 52, 40 (1897).

[7] Micheli: Arch. des Sciences, [4] 10, 122 (1900).

of active and passive iron were different. Müller and Königs-berger[1] concluded from their experiments that, if the passivity were due to an oxide film, the film must be less than one-tenth of a wave-length thick. Later they showed that the re-flecting power of iron mirrors was unchanged when the iron was anode in sodium hydroxide and the current passed until oxygen was evolved (*i. e.*, metal passive) or when as cathode in the same solution, hydrogen was evolved, *i. e.* (metal active).

For sake of comparison, the results of Mott[2] on the thick-ness of the film which is formed on aluminum anodes in saturated solution of disodium phosphate are here given. By determining the increase in weight and knowing the surface over which the film spread, it is possible to deter-mine the thickness of the film. The following results are taken from his paper.

Voltage	Thickness of film	
	If $Al(OH)_3$ cm	If $AlPO_4$ cm
10	0.000013	0.000025
50	0.000032	0.000063
120	0.000064	0.000126

Other methods of measurement gave comparable results indicating that the film is very thin.

One very interesting fact is that the passivity of iron in concentrated nitric acid is overcome by subjecting the iron to the action of a strong magnetic field.[3] Another interest-ing fact is Burgess's[4] application of the passive state of iron in removing the film of brass left on bicycle frames after brazing. A solution of sodium nitrate is used as elec-trolyte and the bicycle frame as anode. The iron becomes passive so does not dissolve while the zinc and copper are

[1] Müller and Königsberger: Phys. Zeit., **5**, 413, 797 (1904). Zeit. Elek-trochemie, **13**, 659 (1907).

[2] Mott: Electrochem. Ind., **2**, 268 (1904).

[3] Nichols: Am. Jour. Sci., [3] **31**, 272 (1886).

[4] Burgess: Trans. Am. Electrochem. Soc., **4**, 31 (1903).

easily soluble.   Burgess believes that the presence of nitrite in solution aids the iron in becoming passive.

The corrosion of iron was studied in the same way as the other metals.   The anodes were made of iron rods and contained small amounts of carbon, manganese and silicon. After electrolysis, the appearance of the anodes and precipitates was as follows.   In both the chloride and sulphate solutions, the anodes were coated with a black film which could be easily removed leaving a bright clean surface.   On the anode, at the surface of the electrolyte a small amount of rust appeared which could be removed completely.   The precipitate was a dirty, olive-green color indicating that most of the metal had dissolved in the ferrous form.   Renault[1] has shown that iron, when in metallic connection with zinc in oxidizing solutions like potassium chlorate or bichromate, acidified with hydrochloric acid, dissolves in the divalent form.   In the nitrate, acetate and tartrate solutions, no precipitate was formed and the only change noted at the anode was the formation of a small amount of rust at the surface of the electrolyte.   The tartrate solution was colored a very faint yellow.   The filtered supernatant electrolyte was alkaline in all cases and no metal was deposited at the cathode.   Special precautions were taken to prevent the iron from rusting after removal from the electrolyte at the end of the run.   The results at room temperature for the larger current are given in the next table.   The efficiency is calculated on the assumption that the iron dissolved in the divalent form.

TABLE XXVII—IRON

At. wt. 55.9; equivalent weight, 27.95
Average anode surface, 13.3 cm^2

Run	Cathode coulometer	100 percent Fe	Time	C. D. amp/dm^2
1	0.4562	0.401	1 hr.	2.9
2	0.497	0.4368	1 hr.	3.2
3	0.5136	0.4514	1 hr.	3.3
4	0.5138	0.4516	1 hr.	3.3

[1] Renault: Ann. Chim. Phys., [4] 11, 150 (1867).

Run	NaCl	Na_2SO_4	$NaNO_3$	$NaC_2H_3O_2$	$Na_2C_4H_4O_6$
1	g. 0.4148_1	0.413_3	0.0036_2	0.001_5	0.0008_4
	% 103.4	103.0	0.9	0.2	0.2
2	g. 0.4542_5	0.4544_3	0.0016_4	0.0_1	0.0016_2
	% 104.0	104.0	0.4	0.0	0.4
3	g. 0.469_5	0.4684_3	0.0038_4	0.0_1	0.002_2
	% 103.9	103.8	0.8	0.0	0.4
4	g. 0.4668_1	0.4572_2	0.0014_4	0.0016_5	0.0028_3
	% 103.3	101.3	0.3	0.3	0.6

The results show that the iron dissolved quantitatively in both the chloride and sulphate solutions and remained passive in the nitrate, acetate and tartrate solutions.

The corrosion in the more dilute solution was then studied. The electrolysis was run at room temperature with the larger current. Only those electrolytes in which the iron was passive in the more concentrated solution were studied. The change in concentration did not overcome the passivity as the results which are given in the next table show.

TABLE XXVIII—IRON

Run	Cathode coulometer	100 percent Fe	Time	C. D. amp/dm²
1	0.2726	0.2396	1 hr.	1.7
2	0.3075	0.2703	1 hr.	1.9
3	0.4587	0.4031	1 hr.	2.9

Run	$NaNO_3$	$NaC_2H_3O_2$	$NaC_2H_3O_2$ (75 g. per liter)	$Na_2C_4H_4O_6$
1	g. 0.0017_6	0.0008_3		0.0008_1
	% 0.7	0.3		0.3
	g. 0.0005_7			
	% 0.2			
	g. 0.0015_6			
	% 0.6			
2	g. 0.0023_3	0.0013_1	0.0021_5	0.0014_7
	% 0.9	0.5	0.78	0.5
3	g. 0.0046_6	0.0014_1	0.0025_3	0.0035_1
	% 1.1	0.3	0.62	0.9
	g. 0.0011_7			
	% 0.3			

With the smaller current, the appearance of the anodes and precipitate was about the same as with the larger. The distinctive fact was that with this lower current density the iron dissolved quantitatively in the nitrate solution. Gee[1] has shown that iron dissolves quantitatively in half-normal sodium nitrate until a current density of 3.5 amp/dm² is reached and then with higher current densities it becomes passive. The appearance of the anode and precipitate was about the same as with the chloride and sulphate solutions. The filtered electrolyte was alkaline and no metal was deposited on the cathode. The results at room temperature are given in the next table.

TABLE XXIX—IRON

Run	Cathode coulometer	100 percent Fe	Time	C. D. amp/dm²
1	0.1871	0.1644	5 hr.	0.24
2	0.2055	0.1806	5 hr.	0.26
3	0.2208	0.1941	5 hr.	0.28
4	0.2782	0.2445	5 hr.	0.35

Run	NaCl	Na₂SO₄	NaNO₃	NaC₂H₃O₂	Na₂C₄H₄O₆
1	g. 0.1761₃	0.1701₁	0.1669₅	0.0005₆	0.0007₃
	% 108.4	103.4	101.5	0.3	0.4
2	g. 0.1886₅	0.1882₄	0.1782₃	0.001₁	0.003₂
	% 104.4	104.2	98.7	0.5	1.7
3	g. 0.1998₁	0.2014₂	0.1934₃	0.0006₅	0.0018₄
	% 102.9	103.8	99.7	0.3	0.9
4	g. 0.2518₁	0.2462₃	0.2436₂	0.001₅	0.0018₄
	% 102.8	100.7	99.6	0.4	0.7

With the current density at which iron dissolved quantitatively in the nitrate solution, it remained passive in the acetate and tartrate solutions. Arth[2] has shown that iron, in a solution of sodium acetate (50 grams per liter) acidified with 50 grams of glacial acetic acid, dissolves quantitatively with a low current density (about 0.009 amp/dm²). He

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[1] Gee: Jour. Inst. Elect. Eng., **41**, 425 (1908).
[2] Arth: Bull. Soc. chim. Paris, [3] **21**, 766 (1899).

also showed that the iron dissolved in the divalent form by adding potassium ferricyanide to the solution directly around the anode. In light of this work of Arth's, it was hoped that a further reduction of the current would cause the iron to dissolve quantitatively in these two solutions. Several attempts with currents of 0.0025–0.003 amperes failed to show any appreciable increase of the corrosion in the unacidified acetate solution. It was noted, however, that in the tartrate solution the corrosion was greater than the theoretical value. The results for electrolysis at room temperature with the more concentrated solution are given in the next table.

TABLE XXX—IRON

Run	Cathode coulometer	100 percent Fe	Time	C. D. amp/dm^2
1	0.0245	0.0215	10 hr.	0.020
2	0.0313	0.025	10 hr.	0.025
3	0.0435	0.0382	10 hr.	0.028
4	0.0505	0.0444	10 hr.	0.032
5	0.0575	0.0505	10 hr.	0.036

Run	$NaC_2H_3O_2$	$Na_2C_4H_4O_6$	$NaNO_3$
1	g. 0.0008$_2$ % 3.7	0.026$_4$ 120.8	
2		0.0018$_5$ 6.5 0.0376$_2$ 136.7 0.0372$_1$ 135.2	0.0367$_6$ 133.4 0.0340$_7$ 123.6
3		0.0$_4$ 0.0 0.0434$_2$ 113.5	
4	g. 0.0005$_4$ % 1.1	0.06$_2$ 135.2	
5		0.0598$_6$ 118.4 0.0609$_7$ 120.5 0.0602$_2$ 119.1 0.0609$_1$ 120.4	0.0489$_5$ 96.7

The explanation for this excess corrosion in the tartrate solution is found in the fact that iron is appreciably soluble in the tartrate solution and the chemical corrosion therefore aids the electrochemical. When the iron anodes were subjected to the action of the tartrate solution for the same length of time that the run occupied, it was found that the iron was dissolved in amounts which are shown in the next table.

TABLE XXXI—IRON

Chemical corrosion in sodium tartrate solution, *i. e.*,
(Amount of iron dissolved by sodium tartrate solution in 10 hours)

Run	Time	Electrode	$Na_2C_4H_4O_6$				
			1	2	3	4	5
1	10 hr.		0.0101 g.	0.0093 g.			0.0115 g.
2	10 hr.		0.0095 g.	0.0095 g.	0.0115 g.	0.0101 g.	0.0118 g.
			6	7			
1	10 hr.		0.0104 g.	0.0091 g.			
2	10 hr.						

If the quantity of iron dissolved chemically is deducted from the total amount lost by corrosion, it will be found that the corrosion then becomes very nearly theoretical. This is shown by two examples which follow.

              Electrode 2
    Run 2   0.0376 g. — 0.0095 = 0.0281 g.   102.2 %
              Electrode 6
    Run 5   0.0598 g. — 0.0104 = 0.0494 g.   97.75 %

The high corrosion in the nitrate solution was doubtless due to the solubility of the iron in the solution although this was not checked by experiment.

Cadmium

The electrolytic corrosion of cadmium was studied in the same manner as the other metals. Its behavior as anode showed many interesting points. The cadmium used was very

pure and contained only traces of zinc and lead. After electrolysis, the appearance of the anodes and precipitates was as follows. In the chloride and acetate solutions, the anodes were coated with a layer of white hydroxide under which was a film of dark brown oxide. Both could be easily removed leaving the surface clean and bright. In the sulphate solution, the anode was much like the other two anodes but it could not be so well cleaned because of a slight tendency to pitting and a greater tendency for the hydroxide to adhere. In the nitrate solution, the anode was covered by a white sheath of hydroxide which could be removed readily. Under this sheath, a heavy layer of a gray-colored mass was formed, sometimes extending 3 mm from the anode surface. In the tartrate solution, the anode was clean, smooth and bright except for splotchy films of a golden brown oxide. In all solutions except the tartrate, a white precipitate was formed which was especially heavy in the nitrate solution. In the tartrate solution, there was no precipitate because cadmium hydroxide is soluble in sodium tartrate. The filtered supernatant liquid was alkaline and metal was precipitated in heavy, spongy masses in the sulphate, nitrate and tartrate solutions but in only small amounts in the chloride and acetate solutions. The numerical results with the larger current at room temperature are given in the next table.

TABLE XXXII—CADMIUM

At. wt. 112.4; equivalent weight, 56.2
Average anode surface, 18.1 cm²

Run	Cathode coulometer	100 percent Cd	Time	C. D. amp/dm²
1	0.3726	0.6585	1 hr.	1.7
2	0.470	0.8306	1 hr.	2.2
3	0.501	0.8854	1 hr.	2.3
4	0.5374	0.9497	1 hr.	2.5
5	0.639	1.1293	1 hr.	3.0

TABLE XXXII—(*Continued*)

Run	NaCl	Na_2SO_4	$NaNO_3$	$NaC_2H_3O_2$	$Na_2C_4H_4O_6$
1	g. 0.6648_5	0.6856_4	0.9002_3	0.6654_2	0.6572_1
	% 100.9	104.1	136.7	101.0	99.8
2	g. 0.8324_5	0.8452_4	1.0868_3	0.845_2	0.7636_1
	% 100.2	101.8	130.8	101.7	91.9
3	g. 0.895_1	0.944_5	1.2286_2	0.8968_4	0.8166_3
	% 101.1	106.6	138.8	101.3	92.2
4	g. 0.9556_5	0.8494_3	1.3586_4	0.9026_1	0.9128_2
	% 100.6	89.4	143.1	95.0	96.1
5	g. 1.1404_5	0.9394_3	1.5978_3	1.020_1	1.0576_2
	% 100.9	83.1	112.4	90.3	93.6

The corrosion was very nearly theoretical in all cases except in the nitrate solution in which it was appreciably greater.

One experiment was tried to ascertain how much oxide adhered to the anode by immersing it in acetic acid until all of the oxide was dissolved and then quickly removing and rinsing with water. This gives only an approximation of the actual amount of adhering oxide because some metal will also dissolve. The anodes were run in sodium nitrate solution at room temperature and the loss in grams and the efficiencies both before and after treatment with acetic acid are given in the following table.

TABLE XXXIII—CADMIUM

Run	Cathode coulometer	100 percent Cd	Time	C. D. amp/dm²
1	0.5792	1.0236	1 hr.	2.7

Run	$NaNO_3$			
1	g. 1.4961_1	1.5091_3	1.5068_4	1.489_5
	% 146.2	147.4	147.4	145.4
	Anodes treated with 80 per cent CH_3COOH			
1	g. 1.5178_1	1.5331_3	1.5331_4	1.5156_5
	% 148.3	149.8	149.8	148.1

This table shows that for this experiment, the average loss on treating the anode with acetic acid is 0.0246 gram and the

average increase in corrosion on allowing for this is 2.4 percent. It was more difficult to remove all the adhering oxide from the cadmium anode in the nitrate solution than in any other solution except the sulphate. Therefore, it is likely that the above gain in efficiency is somewhat above the average gain which would be noted if all the anodes were thus treated before final weighing.

The effect of variation of the concentration of the electrolyte on the corrosion in the nitrate and tartrate solutions was also studied. The nitrate was chosen because it gave a corrosion efficiency greater than theoretical; the tartrate because the electrode, at the conclusion of the run, was clean. With the less concentrated tartrate solution, a precipitate was formed. The results with the larger current at room temperature are as follows:

TABLE XXXIV—CADMIUM

Run	Cathode coulometer	100 percent Cd	Time	C. D. amp/dm^2
1	0.3588	0.6341	1 hr.	1.7
2	0.4423	0.7816	1 hr.	2.06

Run	NaNO$_3$ (75 g. per l.)	NaNO$_3$ (25 g. per l.)	Na$_2$C$_4$H$_4$O$_6$ (75 g. per l.)	Na$_2$C$_4$H$_4$O$_6$ (25 g. per l.)
1	g. 0.8627$_4$ % 136.1	0.9599$_2$ 151.4 0.8438$_3$ 133.1	0.5832$_1$ 92.0	0.5055$_5$ 79.7
2	g. 1.1151$_3$ % 142.7	0.969$_2$ 124.0 1.0749 134.4	0.7481$_5$ 95.7	0.5873$_1$ 75.1

The results show that the corrosion was slightly less in the more dilute solution of the nitrate and quite appreciably less in the more dilute solution of the tartrate. The latter may be explained by the fact that a precipitate was formed in this solution and the anode was therefore not kept so clean as

with the more concentrated solution and the possibility of corrosion was cut down by the formation of a precipitate on the anode.

Some experiments were also run with the smaller current at room temperature. The appearance of the anodes in the chloride, sulphate and acetate solutions was about the same as in the previous case. In the nitrate solution, there was a much smaller quantity of the gray mass than with the larger current. In the tartrate solution, the anode was not so smooth and did not have the golden brown splotches observed with the other current strength. The results as regards deposition of metal at the cathode and alkalinity of the filtered supernatant liquid were strictly comparable to the results in the first case. The results are given in the following table:

TABLE XXXV—CADMIUM

Run	Cathode coulometer	100 percent Cd	Time	C. D. amp/dm^2
1	0.2218	0.392	5 hr.	0.21
2	0.2349	0.4248	5 hr.	0.22
3	0.2415	0.427	5 hr.	0.23
4	0.2616	0.4623	5 hr.	0.25

Run		NaCl	Na$_2$SO$_4$	NaNO$_3$	NaC$_2$H$_3$O$_2$	Na$_2$C$_4$H$_4$O$_6$
1	g.	0.3978$_1$	0.3964$_5$	0.3788$_2$	0.4004$_4$	0.4086$_3$
	%	101.5	101.1	96.6	102.1	104.3
2	g.	0.420$_1$	0.4206$_5$	0.4062$_2$	0.4236$_4$	0.4272$_3$
		98.9	99.0	95.6	99.7	101.0
3	g.	0.436$_1$	0.4404$_4$	0.3870$_3$	0.4400$_5$	0.4576$_2$
	%	102.1	103.1	90.6	103.0	107.9
4	g.	0.4739$_1$	0.475$_3$	0.3782$_5$	0.4798$_2$	0.482$_4$
	%	102.5	102.7	81.8	103.8	104.3

A comparison of these results with those obtained with the larger current shows that in the chloride solution, the corrosion was about the same in both cases. With the acetate and sulphate solutions, it was a trifle higher and with the tartrate solution appreciably higher with the smaller current. On

the other hand with the nitrate solution, it was markedly lower with the smaller current.

The most striking fact noted in this work on cadmium was the high corrosion efficiency in the nitrate solution. The question arose as to whether this was a property peculiar to sodium nitrate alone or whether it was also shared by other nitrates. To settle this question some experiments were run with cadmium nitrate (75 grams per liter) and ammonium nitrate (75 grams per liter). With the former, no precipitate was formed except that which falls from the anode, large amounts of spongy metallic cadmium are deposited at the cathode, and the solution remained neutral. At the anode, large quantities of the gray mass were formed without the intervention of an hydroxide. The solution also contained a large quantity of nitrite. The results with cadmium nitrate at room temperature with the larger current are given in the next table. In Run 1, two anodes were run in sodium nitrate solutions of the two concentrations for purposes of comparison.

TABLE XXXVI—CADMIUM

Run	Cathode coulometer	100 percent Cd	Time	C. D. amp/dm^2
1	0.4999	0.8835	1 hr.	2.3
2	0.4455	0.7873	1 hr.	2.1

Run	NaNO$_3$ (75 g. per l.)	NaNO$_3$ (25 g. per l.)	Cd(NO$_3$)$_2$ (75 g. per l.)
1	g. 1.2709$_5$ % 143.8	1.2590$_1$ 142.5	1.2462$_2$ 141.0 1.2491$_3$ 141.4 1.2583$_4$ 142.4

Run	Cd(NO$_3$)$_2$				
2	g. 1.1179$_1$ % 142.0	1.1364$_2$ 144.3	1.1470$_3$ 145.7	1.1375$_4$ 144.5	1.1499$_5$ 146.1

The corrosion in the cadmium nitrate solution was about the same as in the sodium nitrate, indicating that the large corrosion noted is a property of the nitrates and not of sodium nitrate alone.

The corrosion in ammonium nitrate was next studied at room temperature with the larger current. In the first experiment, solutions of sodium and cadmium nitrates were run for comparison. In the ammonium nitrate, the anode was covered with a black, slimy precipitate which was removed easily and left the surface darkened. No precipitate was formed because cadmium hydroxide is soluble in ammonium salts. The filtered electrolyte was strongly alkaline, a strong odor of ammonia was apparent and nitrite was formed in large quantities.

TABLE XXXVII—CADMIUM

Run	Cathode coulometer	100 percent Cd	Time	C. D. amp/dm²
1	0.5407	0.9554	1 hr.	2.5
2	0.4083	0.7216	1 hr.	1.9
3	0.5373	0.9496	1 hr.	2.5
4	0.6134	1.084	1 hr.	2.8

Run	$NaNO_3$	$Cd(NO_3)_2$	NH_4NO_3
1	g. 1.3727_5 % 143.6	1.3523_1 141.5	2.2988_6 240.6 2.2224_4 232.6

Run	NH_4NO_3				
2	g. 1.8785_1 % 260.3	1.7497_2 242.5	1.7413_3 241.3	2.1890_4 303.4	1.5708_5 217.7
3	g. 2.4996_6 % 263.2	2.0223_2 213.0	1.9405_3 204.4	2.4107_4 253.9	1.7554_4 184.9
4	g. 2.2434_1 % 206.9	2.1455_2 197.9	2.2529_3 207.8	2.6590_4 245.3	2.3414_5 216.0

This large excess corrosion led to the suspicion that the ammonium nitrate itself had a marked corrosive action

on the cadmium. Therefore, some experiments were tried in which weighed test pieces were subjected, with constant stirring, to the action of ammonium nitrate (75 grams per liter). No current was used in this group of experiments. The results showed that cadmium dissolved very readily in the nitrate solution forming, according to Morin,[1] $Cd(NO_3)_2.H_2O.2NH_4NO_3.CdO(NH_3)_2$, a crystalline compound which is readily decomposed by water with the precipitation of cadmium oxide. The test piece was covered with a black, slimy mass similar to that which appeared on electrolysis, the solution became strongly alkaline, a strong odor of ammonia was noted and nitrite was again formed in large quantities. In short, the behavior was exactly analogous to the behavior on electrolysis. The results are given below.

TABLE XXXVIII

Chemical corrosion of cadmium in ammonium nitrate solution
(Anodes used as test pieces)

Run	Time	2	3	4	5	6
1	1 hr.	1.4704 g.	1.488 g.	1.2157	1.3389	1.7909
2	1 hr.	1.6043 g.	1.6686 g.	1.9339	1.6669	1.1310

The above table gives some idea of the amount of cadmium which dissolves in ammonium nitrate in an hour. If this loss is deducted from the total loss by corrosion during electrolysis, the true electrochemical loss will be rather small.

Other ammonium salts show a similar behavior but do not dissolve so much cadmium as the nitrate. The chemical corrosion in the ammonium salts (75 grams per liter) was as follows:

TABLE XXXIX
(Anodes used as test pieces)

Run	Time	NH_4Cl	$(NH_4)_2SO_4$	NH_4NO_3	$NH_4C_2H_3O_2$	$(NH_4)_2C_4H_4O_6$
1	24 hrs.	0.1055₂	0.1213₅	7.8882₂	0.1028₁	0.0857₃
2	12 hrs.	0.0634₃	0.0536₄	7.0914₅	0.0633₁	0.0550₂

In all the solutions except the nitrate, the test piece was

[1] Tommasi: Electrochimie, 217.

coated with a small amount of black or brown oxide which could be easily removed leaving the surface clean and bright. The appearance in the nitrate solution has already been described. In all the solutions except the nitrate, the corrosion in the 24-hour run was much greater than in the 12-hour. In the nitrate solution, the formation of the black oxide coating served to protect the test piece against further corrosion and the amount dissolved in the longer run was not much greater than that dissolved in the shorter.

Some experiments were also made using solutions of cadmium and sodium nitrates acidified with various amounts of nitric acid (25 cc HNO_3 1.4 sp. gr. per liter) to see if the gray compound was formed in acid solutions. It was found only in the sodium nitrate solution containing 50 cc of acid. For comparison, runs were also made in nitric acid of this concentration. The high current efficiency was due to chemical corrosion aiding the electrochemical as shown by the fact that in 1 hour, 2.9146 grams of cadmium was dissolved in nitric acid of this concentration. If this amount is deducted from the loss during electrolysis, the current efficiency in nitric acid in run 1 is only 42.85 percent. The results with nitric acid in the two runs are not strictly comparable because the time was not the same. The results at room temperature with the larger current are given in the following table.

TABLE XL

Run	Cathode coulometer	100 percent Cd	Time	C D. amp/dm^2
1	0.5138	0.908	1 hr.	2.4
2	0.4293	0.7587	$^3/_4$ hr.	2.7

Run	Cd(NO$_3$)$_2$ 150 cc HNO$_3$ 50 cc	Cd(NO$_3$)$_2$ 100 cc HNO$_3$ 100 cc	NaNO$_3$ 150 cc HNO$_3$ 50 cc	NaNO$_3$ 100 cc HNO$_3$ 100 cc	HNO$_3$ 200 cc
1	g. 1.4543$_2$ % 160.2	2.0445$_3$ 225.2	1.4906$_4$ 164.1	1.888$_1$ 207.9	3.2948$_5$ 362.9
2	g. 1.195$_2$ % 147.5	1.1830$_3$ 155.9	1.1390$_5$ 150.1	1.1774$_1$ 155.2	1.7188$_4$ 226.5

In the electrolysis of the nitrate solutions, nitrite was always formed. There was a possibility that in the nitrate solution the corrosion might be greater than in the nitrate or that the nitrite might itself have a marked solvent action on the metal. The latter conjecture, however, will not explain the excess corrosion because only 0.0088 g of cadmium was dissolved chemically by sodium nitrite in an hour. A run was made using sodium nitrite (75 grams per liter) as electrolyte. At the conclusion of the run, the anodes were found to be covered with a white coating under which some black non-adherent oxide was formed. After these had been removed, the surface was fairly clean. A white precipitate was formed, the filtered supernatant liquid was alkaline, and a faint odor of ammonia was noted. The larger current was used and the experiment was carried on at room temperature.

TABLE XLI—CADMIUM

Run	Cathode coulometer	100 percent Cd	Time	C. D. amp/dm^2
I	0.5533	0.9778	1 hr.	2.6

Run	NaNO$_2$				
I	g. 0.9915$_1$	0.9923$_2$	0.998$_3$	0.9975$_5$	0.9915$_6$
	% 101.4	101.5	102.0	102.0	101.4

The corrosion was very much less than with the nitrate so the formation of nitrite will not account for the excess corrosion.

With copper, it is easy to account for any excess corrosion since we know that there is always a tendency for copper to dissolve as the cuprous salt. If cadmium and tin formed compounds with a valence of one, it would be easy to account for this excess corrosion. As stated before, no reference to tin with a valence of one could be found. However, it is known that cadmium sometimes forms compounds in which the valence is less than two. Marchand[1] found on heating

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[1] Marchand: Pogg. Ann., **38**, 145 (1836).

cadmium oxalate in a closed vessel that a green powder, which he thought was Cd_2O, was formed. Souchay and Lenssen[1] thought that this was not a compound but a mixture of cadmium and cadmium oxide although Marchand was unable to extract any cadmium by shaking with mercury. Morse and Jones[2] described a compound Cd_4Cl_7 which was made by heating metallic cadmium with cadmium chloride in an atmosphere of nitrogen. They also describe the preparation of Cd_4Br_7 and $Cd_{12}I_{23}$. When these compounds are treated with water, a grayish white, amorphous precipitate which was supposed to be CdOH is formed. It was impossible to isolate this compound because of its instability. Canzoneri[3] heated metallic cadmium and cadmium chloride together with the hope of obtaining a subchloride of cadmium, CdCl, which should be analogous to mercurous chloride since cadmium and mercury are in the same group of the periodic table. He obtained a lead-gray powder the composition of which depended on the relative amounts of cadmium and cadmium chloride used. If the chloride was in excess the gray powder had the composition $2CdO.CdCl_2$. On fusing cadmium oxide and chloride, a heavy white compound of the same composition was formed with evolution of heat. If the metal was in excess, the product contained relatively more cadmium than required for the composition $2CdO$. $CdCl_2$. This gray compound was insoluble in water but was decomposed by it into metallic cadmium and cadmium chloride. The products of the decomposition depend on the temperature and the proportions of substances used in its preparation. Tanatar[4], on heating cadmium oxalate in a stream of dry carbon dioxide, obtained a green, amorphous powder which has the composition Cd_4O. Tanatar and Levin[5], on heating equal parts of cadmium hydroxide and

[1] Souchay and Lenssen: Liebig's Ann., 103, 314 (1857).

[2] Morse and Jones: Am. Chem. Jour., 12, 488 (1890).

[3] Canzoneri: Gazz. chim. ital., 27, 486 (1897).

[4] Tanatar: Zeit. anorg. Chem., 27, 432 (1901).

[5] Tanatar and Levin: Centralblatt., 1902, II, 564.

cadmium oxalate in the presence of water up to 130°–140°, obtained a green powder which they believed to be Cd_3O_2. The same workers, on heating two parts of the oxalate with one part of the hydroxide under the same conditions as before, obtained another green powder which they believed had the composition Cd_2O and which on heating with water or out of contact with air gave metallic cadmium and cadmium oxide. Tanatar also showed that the heat evolved on treating gram molecular quantities of these oxides with dilute acids was less than that evolved on treating a gram molecule of cadmium oxide with acids of the same concentration. Denham[1] showed that cadmium was dissolved by cadmium sulphate in the warm limb of the "circulation apparatus" and deposited in the cold arm. Apparently the cadmium behaves like copper and forms a cadmous sulphate which is unstable at low temperatures, and breaks down, giving metallic cadmium and cadmium sulphate. The equation may be represented as follows

$$Cd + CdSO_4 \rightleftarrows Cd_2SO_4.$$
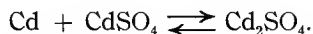
All this seems to indicate that cadmium with a valence of one is fairly authentic.

The possible analogy between copper and cadmium suggested by Denham's experiments made it possible that when cadmium was made anode in a 30 percent solution of sulphuric acid and the solution electrolyzed, using a high current density, it would behave as copper did under the same conditions. Fischer[2] showed that when copper wire was made anode in "best conducting sulphuric acid," *i. e.*, sulphuric acid of the above concentration, a high anode current density caused the formation of a cloud of pulverulent metallic copper which came from the decomposition of the cuprous sulphate formed at the anode. On repeating this experiment with cadmium, no pulverulent metallic cloud was formed but the cadmium dissolved leaving a very smooth, polished surface.

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[1] Denham: Loc. cit.
[2] Fischer: Zeit. phys. Chem., **48**, 177 (1904).

However, the experiment was tried by simply duplicating the conditions in the copper experiment. There is a possibility that, under proper conditions of acid concentration and anode current density, the metallic cadmium might be formed but there is at present no experimental data to prove or disprove this conjecture.

The compound which formed on the anode was grayish white and heavier than the ordinary cadmium hydroxide which could be "floated off" by water. No metallic cadmium could be separated from it by shaking with mercury and it dissolved in hydrochloric acid without evolution of gas, which was another indication that no uncombined metal was present in the substance. It was, however, impossible to prove the composition of the substance because it was unstable and broke down easily. And it would be difficult to obtain by electrolysis a sample of the substance which was entirely free from the cadmic hydroxide. But when the fact is taken into account that mercury, which is the closest chemical analogue of cadmium has two oxides Hg_2O and HgO, it is reasonable to suppose that cadmium should also have two oxides similar in constitution to those of mercury.

Denham has shown that heat favors the formation of the cadmous compound. Therefore, the effect of electrolyzing nitrate solutions heated to $95°$ was tried. The results were much the same as when the electrolysis was run at room temperature except that the gray substance did not adhere to the electrode but fell off and collected at the bottom of the cell. Nitrite was formed, spongy metal was deposited at the cathode and the filtered supernatant liquid was alkaline. The results are given in the following table and show that the corrosion efficiency was increased by increasing the temperature.

TABLE XLII—CADMIUM

Run	Cathode coulometer	100 percent Cd	Time	C. D. amp/dm²
1	0.6861	1.0358	1 hr.	2.7
2	0.6258	1.1059	1 hr.	2.9

Run	$NaNO_3 - 95°$			
1	g. 1.5369_1	1.5313_2	1.4906_3	1.541_4
	% 148.4	147.8	143.9	148.7
2	g. 1.6676_1	1.6539_5	1.6393	1.7446_4
	% 150.8	149.5	148.2	157.8

The effect which a change of current density has on the corrosion efficiency in nitrate solutions at room temperature was next tried. The results are given in the next table.

TABLE XLIII—CADMIUM

Run	Cathode coulometer	100 percent Cd	Time	C. D. amp/dm²
1	0.1057	0.1868	1 hr.	0.49
2	0.1177	0.2081	1 hr.	0.55
3	0.1311	0.2317	1 hr.	0.61
4	0.2618	0.4627	1 hr.	1.2
5	0.2415	0.4268	1 hr.	1.1
6	0.4745	0.8386	1 hr.	2.2
7	1.5048	2.6594	1 hr.	7.0
8	2.7497	4.8595	1 hr.	12.8
9	2.7465	4.8538	1 hr.	12.8

Run	$NaNO_3$				
1	g. 0.2289_1	0.2212_2	0.2345_3	0.2236_4	0.2347_5
	% 122.5	118.4	125.5	119.6	125.6
2	g. 0.2432_1	0.2401_2	0.2449_3	0.2519_4	0.2519_5
	% 116.9	115.4	117.7	121.1	121.1
3	g. 0.2937_1	0.2819_2	0.2923_3	0.2975_4	0.2936_5
	% 126.8	121.6	126.2	128.4	126.7
4	g. 0.6557_1	0.6617_2	0.6807_3	0.6753_4	0.6736_5
	% 141.7	143.0	147.1	146.0	145.6
5	g. 0.5903_1	0.6146_2	0.6038_3	0.608_6	0.6135_5
	% 138.2	144.0	141.1	142.4	143.7
6	g. 1.1722_6	1.1799_7	1.1752_8	1.1949_9	1.1959_{10}
	% 139.8	140.8	140.1	142.5	140.2
7	g. 4.3706_6	4.2952_7	4.2743_8	4.4252_9	4.3398_{10}
	% 164.3	161.5	160.7	166.4	163.2
8	g. 8.4377_6	8.4005_7	8.3672_6	8.4398_9	8.4860_{10}
	% 173.6	172.9	172.2	173.7	174.6
9	g. 8.244_6	8.3920_7	8.2297_8	8.2934_9	8.3952_{10}
	% 169.9	172.9	169.6	170.9	173.0

These results show that the corrosion is markedly increased by increasing the current density. This means, no doubt, that a high current density at the anode favors the formation of the cadmous compound.

Attention has been called to the fact that nitrite was always formed when a solution of nitrate was electrolyzed. The greater part of the nitrite will, of course, come from cathodic reduction. The questions arose as to whether any nitrite was formed by the reaction which took place at the anode, especially since the cadmous compounds are said to possess marked reducing power and furthermore, whether an alkali was necessary for the formation of the gray oxide. The experiments with cadmium nitrate indicated that the presence of an alkali was not necessary to bring about its precipitation. To answer these questions, some experiments were tried with the anode and cathode compartments separated by a porous cup. The cadmium anode in sodium nitrate was placed in the anode compartment and the platinum wire cathode in the cathode compartment. As cathode liquid several different solutions were used. First, sodium nitrate acidified with nitric acid was tried but the objections were that both sodium hydroxide and sodium nitrite would be formed in the cathode compartment and their anions would move to the anode. Then dilute nitric acid was tried and the solution was kept acid by constant addition of nitric acid during the electrolysis. While this overcame the first objection it did not overcome the second because the anions of nitrite, which was formed in the cathode compartment, would migrate into the anode compartment and it was one of the objects of the experiment to see if any nitrite was formed by the action of the gray oxide on sodium or cadmium nitrates. Furthermore, the nitric acid might diffuse into the anode compartment and attack the anode chemically. The nascent hydrogen thus liberated would have a marked reducing effect on the nitrate present. When these two solutions were used as cathode liquid, nitrite was found in the anode compartment and the gray substance was formed on

the anode. The corrosion efficiency in these runs was about the same as when the anode and cathode compartments were not separated. The results are given in the following table.

TABLE XLIV—CADMIUM

Run 1. Cathode in $NaNO_3$ acidified with HNO_3

Run 2. Cathode in dilute HNO_3—kept acid throughout the run.

Run	Cathode coulometer	100 percent Cd	Time	C. D. amp/dm²
1	0.5245	0.9267	1 hr.	2.4
2	0.5133	0.9071	1 hr.	2.4

Run	$NaNO_3$			
1	g. 1.2997_1	1.3480_2	1.3152_3	1.3241_4
	% 140.3	145.5	141.9	142.9
2	g. 1.2839_1	1.2958_2	1.3185_3	1.2912_4
	% 141.5	142.8	145.4	142.3

The third solution which was used as a cathode liquid was a saturated solution of copper sulphate. With this solution in the cathode compartment, there will be no great danger of any nitrite being formed in large quantities by cathodic reduction of any nitrate which has diffused into the cathode compartment. Furthermore, any sodium hydroxide formed at the cathode will immediately react with the copper sulphate and cannot diffuse out into the anode compartment and precipitate the cadmium compounds which are formed at the anode. Under these conditions the gray oxide was again formed at the anode and there was also a large quantity of nitrite formed in the anode compartment while none was found in the cathode compartment. The liquid in both compartments remained neutral. Several experiments were tried and the results could be duplicated every time. The results of one quantitative experiment are here given.

TABLE XLV—CADMIUM

Cathode in a saturated solution of $CuSO_4$

Run	Cathode coulometer	100 percent Cd	Time	C. D. amp/dm^2
I	0.5552	0.9812	1 hr.	2.6

Run	NaNO$_3$				
I	g. 1.4352$_1$ % 146.2	1.3521$_2$ 137.8	1.5107$_3$ 153.9	1.4317$_4$ 145.9	1.4380$_5$ 146.3

The results indicated that the formation of this gray compound did cause a reduction of sodium nitrate to sodium nitrite.

Some experiments were tried under the same conditions with copper, tin, and zinc. Cadmium was also run for comparison. With copper, no precipitate except a small amount of cuprous oxide was formed. The anode solution became slightly acid to litmus and no nitrite was found. With zinc, a grayish white gelatinous hydroxide was formed on the anode but it was easily removed leaving the surface clean. The filtered anode liquid was slightly alkaline to litmus and gave a slight test for nitrite. With tin, a heavy white precipitate was formed and the anode was coated with the same gray substance as formed when the electrolysis was run without a cup. The anode, after this substance had been removed, was clean. The filtered anode liquid was slightly acid to litmus and contained no nitrite. The results with cadmium have already been described. In all cases, the copper sulphate in the porous cup remained neutral.

The results are given in the following table.

TABLE XLVI

Cathode in saturated solution of CuSO$_4$. Time one hour

Run	Cathode coulometer	Anode metal	100 percent corrosion	C. D. amp/dm^2	NaNO$_3$
1	0.4057	Cd	0.717	1.9	g. 1.0248$_2$ % 142.9
		Cu	0.4057	1.9	g. 0.4203$_3$ % 103.6
		Sn	0.7601	2.2	g. 1.360$_6$ % 178.9
		Zn	0.4172	2.7	g. 0.4187$_1$ % 100.3
2	0.5932	Cd	1.0484	2.7	g. 1.3194$_2$ % 125.9
		Cu	0.5932	2.7	g. 0.6098$_7$ % 102.8
		Sn	1.1098	3.2	g. 1.926$_6$ % 173.5
		Zn	0.610	4.0	g. 0.5914$_1$ % 97.2

The efficiency of corrosion was about the same or perhaps a trifle less than when the anode and cathode are not separated by the cup.

In order to show whether or not nitrite was formed when metals were placed in nitrate solutions, zinc, copper, nickel, tin, iron and cadmium were placed in nitrate solutions which were free from nitrite and set aside for a week in beakers covered with cover glasses but to which air had free access. At the end of the week, zinc gave the best test for nitrites, cadmium a good test, iron only a fair test, while copper, nickel and tin gave no test at all. This experiment was repeated and the same results were obtained, indicating that the current was not necessary to bring about the reduction of nitrate to nitrite.

Summary

In this work, the electrolytic corrosion of zinc, copper, nickel, tin, iron and cadmium was studied in solutions of sodium chloride, sulphate, nitrate, acetate and tartrate containing 75 grams of salt per liter. The results showed that the

metals corroded to different extents in the different solutions, although some corroded to about the same extent in two and sometimes in three electrolytes. The corrosion was found in some cases to approximate closely to the theoretical amount, in others to be very much less and in still others to be very much greater than the theoretical. When the corrosion was less than theoretical, it was found that further electrolytic action was prevented by the formation of an oxide or hydroxide film on the anode. In some cases, notably copper and tin in the tartrate solution, the formation of this film caused a marked increase in the resistance of the circuit. When the corrosion was greater than theoretical, the excess corrosion was not due to any appreciable extent to loss of metal by mechanical disintegration, although there will always be some slight loss due to this cause but never enough to account for any large excess. The excess corrosion may then be due to the formation of compounds in which the valence is less than the lowest ordinary valence of the metal. It is known that there is always a tendency for copper to dissolve to some extent in the cuprous form and in cases where the corrosion was greater than theoretical with copper anodes the presence of some cuprous salts could always be shown. To explain the large excess corrosion of tin and cadmium in sodium nitrate solution the existence of "subvalent" forms of these metals (*i. e.*, valence of one) has been postulated.

The effect of changing the concentration from 75 to 25 grams per liter was tried and it was found that the differences in corrosion in the two solutions were in general very small. However, change of concentration of the tartrate solution did sometimes lead to precipitation with the more dilute solution whereas with the more concentrated no precipitate was formed. Any decrease in corrosion noted was due to the fact that the insoluble film was formed more quickly in the dilute solution or in other words the conditions for the metal becoming passive were improved.

The effect of decreasing the current density was also studied and the results showed that with some metals, the

corrosion in the same solution was increased by a decrease of the current density while with other metals, it was decreased and with still others, it was little affected one way or the other. On the other hand with cadmium in the sodium nitrate solution, it was found that the corrosion was markedly increased by increase of the current density.

Increase of temperature was also shown to have an effect on the corrosion of copper in some of the solutions although the formation of a heavy layer of cuprous oxide on the anodes in some of the solutions prevented a very pronounced increase. With cadmium in sodium nitrate solution, the corrosion was appreciably greater at the higher temperatures.

In nearly all solutions, the filtered supernatant liquid was alkaline after electrolysis and in some solutions metal was deposited at the cathode. This metal may come from reduction of the metallic hydroxides by the nascent hydrogen at the cathode or from the electrolytic decomposition of basic salts. In some cases, the amount of metal thus deposited was large.

The electrolyte and the precipitated hydroxide were subjected to the action of any gases which were liberated at the electrodes. Thus there will always be a tendency to reduction at the cathode and it was found that nitrite was always formed on the electrolysis of nitrates and that the quantity of nitrite formed, depended in some measure on the metal used as anode. Experiments were also tried to see how the nitrite affected the corrosion of the metal both chemically and electrochemically and it was found that the excess corrosion in the nitrate solution could not be accounted for by the action of the nitrite. On the other hand if the metal went passive, oxygen was liberated at the anode and the electrolyte was subjected to oxidation which might change its chemical nature and bring about further changes in the products of the electrolysis. Such a case was found when copper went passive in the tartrate solution and the tartrate was oxidized with the formation of formic acid which in

alkaline solution reduced the cupric compounds to cuprous hydroxide. Furthermore with a nickel anode, the solution was changed by oxidation to a dark brown liquid.

In some cases, excess corrosion may be explained by the solvent action of the electrolyte on the anode metal, the chemical corrosion working with the electrochemical to give a total loss which exceeds the theoretical.

A very important factor was the electrode surface and care was taken to file and scour each anode with carborundum paper before beginning the electrolysis to insure a new and clean surface for each run. Even then, it was impossible to duplicate the results exactly. Experiments with freshly deposited copper showed that there were discrepancies in the results even with this precaution to insure a uniform anode.

This work was suggested by Professor Bancroft and carried on under his supervision. This opportunity is taken to thank him for his kindly interest in the work and for the many fruitful suggestions he made during its progress.

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